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	[Inventor]	
10	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
	[Name]	Shigeru Emoto
	[Inventor]	
	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
15	[Name]	Toshiki Nanya
	[Inventor]	
	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
20	[Name]	Naohito Shimota
	[Inventor]	
	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
	[Name]	Maiko Kondo
25	[Inventor]	
	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
	[Name]	Shinichiro Yagi
	[Inventor]	
30	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
	[Name]	Hiroto Higuchi
	[Inventor]	

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	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
	[Name]	Fumihiko Sasaki
	[Inventor]	
5	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
	[Name]	Takahiro Honda
	[Inventor]	
10	[Address]	c/o Ricoh Company, Ltd. 3-6, Nakamagome 1-chome, Ota-ku, Tokyo
	[Name]	Junichi Awamura
	[Applicant]	
	[Id. No.]	000006747
	[Name]	Ricoh Company, Ltd.
15	[Representative]	Masamitsu Sakurai
	[Agent]	
	[Id. No.]	100105681
	[Patent Attorney]	
	[Name]	Hidehiko Takei
20	[Application Fee]	
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[Claim 1]

Toner used for an image forming method employing a toner recycling system, and containing at least a modified polyester resin, a colorant, and a releasing agent, characterized in that a  
5 surface of the toner is coated with a fine particle polymer, a volume average particle diameter (Dv) of the toner is 4.0 to 6.0  $\mu\text{m}$ , a ratio Dv/Dn of the volume average particle diameter (Dv) and a number average particle diameter (Dn) is 1.00 to 1.30, and a shape factor SF-1 of the toner is 140 to 200.

10 [Claim 2]

The toner as described in claim 1, characterized in that a ratio Dv/Dn of the toner is 1.00 to 1.20.

[Claim 3]

15 The toner as described in claim 1 or 2, characterized in that a shape factor SF-1 of the toner is 150 to 180.

[Claim 4]

The toner as described in any one of claims 1 to 3, characterized in that a glass transition point of the fine particle polymer is 50 to 110  $^{\circ}\text{C}$ .

20 [Claim 5]

The toner as described in any one of claims 1 to 4, characterized in that an average particle diameter of the fine particle polymer is 10 to 200.

[Claim 6]

25 The toner as described in any one of claims 1 to 5, characterized in that particles of the toner having an equivalent circle diameter of 2  $\mu\text{m}$  or smaller are 1 to 15 % by number.

[Claim 7]

30 The toner as described in any one of claims 1 to 6, characterized in that average circularity of the toner measured with a flow type particle image analyzer is 0.90 to 0.95.

[Claim 8]

The toner as described in any one of claims 1 to 7,

characterized in that the toner is obtained by dissolving or dispersing, in an organic solvent, a composition containing at least resin reactive with a compound having an active hydrogen group, a compound having an active hydrogen group, a colorant, and a releasing agent, dispersing a solution or a dispersion liquid of the composition in an aqueous medium, removing the organic solvent after or during reaction of the resin reactive with the compound having the active hydrogen group, and then carrying out washing and drying.

10 [Claim 9]

The toner as described in claim 8, characterized in that a toner component comprising a modified polyester resin reactive with an active hydrogen, a colorant, and a releasing agent is dispersed in an organic solvent in presence of a dispersant, a resultant dispersion liquid is reacted with a cross-linking agent and/or an extender in an aqueous medium, a resultant dispersion liquid is stirred in a stirring tank including a stirrer having a peripheral speed of 5 m/s or more to change a spherical particle to a spindle shape, and then the solvent is removed from the dispersion liquid.

[Claim 10]

The toner as described in claim 8 or 9, characterized in that a glass transition point of the polyester resin contained in the toner is 40 to 70 °C.

25 [Claim 11]

The toner as described in any one of claims 8 to 10, characterized in that an acid value of the polyester resin contained in the toner is 1 to 30 mgKOH/g.

[Claim 12]

30 The toner as described in any one of claims 1 to 11, characterized in that the toner is used for a two-component developer.

[Claim 13]

An image forming apparatus having a transfer means for transferring a toner image carried on a toner image carrier to a transfer material, and a cleaning means for cleaning toner remaining on a surface of the toner image carrier after the transfer by using a blade, characterized by using the toner as described in any one of claims 1 to 12.

[Claim 14]

A process cartridge which integrally supports a photoconductor, and at least one means selected from a group of a photoconductor, a charge means, a development means, and a cleaning means, and is freely attachable to and detachable from an image forming apparatus body, characterized in that the development means holds toner (developer), and the toner (developer) is dry type toner as described in any one of claims 1 to 12.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to toner used for an image forming method employing a recycle system of toner and using electrophotography, electrostatic recording, electrostatic printing, or the like, and a developer used for the toner, a toner container, an image forming apparatus (developing device), and a process cartridge.

[0002]

[Background Art]

In the electrophotography, an electrostatic latent image is formed by a charge and an exposure on a surface of a latent image carrier (hereinafter referred to also as a photoconductor) having a photoconductive layer generally formed of a photoconductive material. Subsequently, the electrostatic latent image is developed by toner formed of coloring particles, and after the obtained toner image is transferred generally to a recording

materials, such as paper, fixed to form a copy image. Although various methods are conventionally known as fixing methods of the toner, a heat roller fixing method is adopted in particular from a viewpoint of high thermal efficiency and high-speed fixing.

5 Following performances, and the like, are basically required for toner applied to the heat roller fixing method.

(1) The toner may be securely fixed at low temperature, i.e., the toner has an excellent low temperature fixing property.

(2) Molten toner is hardly transferred to the heat roller in  
10 fixing, i.e., the toner is required to have an excellent hot offset property, and the like.

Further, to form a clear copy image, the toner is required to stably exist as fine particles without being aggregated in use or a storage environment, i.e., the toner is required to have  
15 excellent storage stability. Moreover, to stably form an excellent image without fogging over many times, such a performance is required that the toner does not easily be crushed due to mechanical impact, pressure, or the like, in a developing device.

20 [0003]

Recently, more image forming apparatuses for developing a latent image formed on a photoconductor by using toner have a cleaner for removing toner remaining on a photoconductive drum after the transfer, and a recycling device for returning the  
25 toner removed by the cleaner to a developing device (for example, refer to patent document 1). However, when the toner is used for the image forming apparatuses using a recycling system, such problems are easily caused as deterioration of image density, scumming of paper, fogging, and adhesion to a carrier with  
30 increase in number of copy images. The problems are caused from toner deformed and destructed by shearing force during a recycling process, and a decline in charge imparting ability of the carrier due to toner fine powder formed simultaneously with a

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decline in charge ability of the toner. Furthermore, wax contained as a releasing agent in a black and white copy in which oilless toner is mainly used bleeds out on a toner particle surface due to heat and cleaning in an image forming apparatus, or toner stress in a toner recycling system, adheres to a carrier, and causes charge deterioration.

[0004]

Toner containing a cross linked polyester resin as a binder resin is known as toner used for such a recycling system (for example, refer to patent documents 2 to 7). However, when the toner frequently receives mechanical external force, such as stirring, in a developing device due to recycling of the toner, toner particles may be destroyed to form fine powder. The fine powder contaminates carrier particles, charge ability of the carrier particles deteriorates, and as a result, toner having an insufficient charge amount is produced, which causes problems that the toner contaminates a developer carrier and other devices, and a developing property deteriorates.

[0005]

In investigation of the recycling system, not only research of the toner but research and development of image forming methods have been made. Various devising and improvement are made also in image forming apparatuses. For example, in an electrostatic image formation process, an attempt to reuse residual toner of an image carrier after an image is transferred to an image receiving medium has been made. The residual toner is stored in a recovery dedicated bottle or the like, and the bottle has been disposed of as industrial waste. Such disposal contaminates an earth environment, and is waste of a resource, which is not preferred. Therefore, toner recycling method for eliminating the disposal of the toner and using the entire toner has been examined.

For example, such techniques are disclosed as a technique of

using recovered toner as a part of refill toner for a developing device by providing a conveyance route for conveying recovered toner from a cleaning device to a developing device (for example, refer to patent document 8), a technique of recovering transfer residual toner in a developing device without providing a cleaning device (for example, refer to patent document 9), and a technique in which a rotary member capable of applying bias is provided to recover toner by electrostatic force when a region of a carrier corresponding to a paper passing part passes, and the toner is caused to adhere to the image carrier when a region corresponding to a part where the paper is not passed through passes (for example, refer to patent document 10).

[0006]

However, the above techniques each have defects, and are not considered as satisfactory. The technique described in patent document 8 requires a conveyance route of toner, such as a pipe, and further a toner conveying means, such as a screw or a belt, which enlarges and complicates an apparatus. In the technique described in patent document 9, the toner once adhered to the image carrier as transfer residual toner is hardly recovered by the developing device, firmly fixed to the image carrier, or often interrupted during image formation, resulting in stain of a background portion and an image area in many cases. Further, the technique is not ready for abnormal circumstances, such as a paper jam, and has often an adverse effect on a step after the image carrier is stained. Various reports have been made in addition to the above descriptions, but are not still satisfactory.

[0007]

Meanwhile, based on a strong market demand for higher image quality, development of an electrophotographic apparatus suitable for the higher image quality and a toner developer used for the apparatus has been further spurred. The toner responding the



higher image quality is preferably toner having a small particle diameter, and spherical toner having narrow particle size distribution. When toner has sharp particle size distribution and is spherical, individual toner particle behaves uniformly in development, and fine dot reproducibility improves remarkably. However, when toner having a diameter smaller than before and a uniform particle diameter is used in the recycling system, the toner encounters a still more disadvantageous situation. In a case of the recycling system, difficulty is first caused regarding cleanability. Stable cleaning of toner having a uniform and small diameter is difficult for blade cleaning. Under such circumstances, methods of improving the cleanability through a device of toner are proposed in various forms. One of the methods suggests change of the toner particle from a spherical to an irregular shape. Powder fluidity of toner is reduced by making the toner in the irregular shape, and the toner is easily stemmed by the blade cleaning. However, when a degree of irregular shape of toner is extremely strengthened, a behavior of toner becomes unstable in development and the like, and the fine dot reproducibility deteriorates.

[0008]

As mentioned above, reliability for cleaning is improved by making the toner in an irregular shape, but on the other hand, a defect is caused in fixing. That is, when the shape of toner is made irregular, packing density of toner in a toner layer on a transfer material before fixing is reduced, thermal conductivity of the toner layer becomes small in fixing, and a low temperature fixing property deteriorates. In particular, when pressure in fixing is smaller than before, the thermal conductivity deteriorates and low temperature fixation is obstructed. For example, although toner formed of a polyester having a degree of sphericity for Wadell practical sphericity of 0.90 to 1.00 is proposed (for example, refer to patent document 11), the toner

has a substantially spherical shape, the problem of cleaning mentioned above is not solved.

[0009]

[Patent document 1] Japanese Patent Laid-open Publication No.  
5 Sho60-41079

[Patent document 2] Japanese Patent Laid-open Publication No.  
Sho59-14144

[Patent document 3] Japanese Patent Laid-open Publication No.  
Sho58-14147

[Patent document 4] Japanese Patent Laid-open Publication No.  
10 Sho60-176049

[Patent document 5] Japanese Patent Laid-open Publication No.  
Sho60-176054

[Patent document 6] Japanese Patent Laid-open Publication No.  
15 Sho62-127748

[Patent document 7] Japanese Patent Laid-open Publication No.  
Sho62-127749

[Patent document 8] Japanese Patent Laid-open Publication No.  
Sho63-246780

[Patent document 9] Japanese Patent Laid-open Publication No.  
20 Hei1-118774

[Patent document 10] Japanese Patent Laid-open Publication No.  
Hei6-51672

[Patent document 11] Japanese Patent Laid-open Publication No.  
25 Hei11-133665 (claim 1, third page, left column, 27th line to 32nd line)

[0010]

[Problems to be Solved]

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The present invention was made in view of such circumstances,  
30 and objects of the present invention are to provide  
(1) toner and a developer which does not cause deformation and  
destruction of toner when employed in a toner recycling system,  
produces only a few change in a surface state of toner, does not

cause deterioration in durability of developer, fogging, deterioration in image density, scumming, an environmental variation in toner, and the like, and may yield excellent image quality, and an image forming apparatus and a removable process cartridge, and

(2) toner and a developer capable of yielding high-definition image quality showing excellent fine dot reproducibility. To provide toner and a developer capable of yielding high reliability in cleaning in particular,

(3) toner and a developer having an excellent low temperature fixing property,

(4) toner and a developer capable of satisfying the above objects (1) to (3), and

(5) toner which has excellent transfer efficiency, leaves little transfer residual toner, and is capable of yielding a high-definition image.

[0011]

[Means for Solving Problems]

A result of having examined wholeheartedly a means for improving the low temperature fixing property as the problem mentioned above, the problem is found to be solvable by using a polyester resin as a main component of a binder resin of toner, and finally, the present invention is completed.

That is, the above problems are solved by following toner according to the present invention. (1) Toner used for an image forming method employing a toner recycling system, and containing at least a modified polyester resin, a colorant, and a releasing agent, characterized in that a surface of the toner is coated with a fine particle polymer, a volume average particle diameter (Dv) of the toner is 4.0 to 6.0  $\mu\text{m}$ , a ratio Dv/Dn of the volume average particle diameter (Dv) and a number average particle diameter (Dn) is 1.00 to 1.30, and a shape factor SF-1 of the toner is 140 to 200. (2) The toner as described in the above item

(1), characterized in that a ratio  $D_v/D_n$  of the toner is 1.00 to 1.20. (3) The toner as described in the above item (1) or (2), characterized in that a shape factor SF-1 of the toner is 150 to 180. (4) The toner as described in any one of the above items (1) to (3), characterized in that a glass transition point of the fine particle polymer is 50 to 110 °C. (5) The toner as described in any one of the above items (1) to (4), characterized in that an average particle diameter of the fine particle polymer is 10 to 200. (6) The toner as described in any one of the above items (1) to (5), characterized in that particles of the toner having an equivalent circle diameter of 2  $\mu\text{m}$  or smaller are 1 to 15 % by number. (7) The toner as described in any one of the above items (1) to (6), characterized in that average circularity of the toner measured with a flow type particle image analyzer is 0.90 to 0.95. (8) The toner as described in any one of the above items (1) to (7), characterized in that the toner is obtained by dissolving or dispersing, in an organic solvent, a composition containing at least resin reactive with a compound having an active hydrogen group, a compound having an active hydrogen group, a colorant, and a releasing agent, dispersing a solution or a dispersion liquid of the composition in an aqueous medium, removing the organic solvent after or during reaction of the resin reactive with the compound having the active hydrogen group, and then performing washing and drying. (9) The toner as described in the above item (8), characterized in that a toner component containing a modified polyester resin reactive with an active hydrogen, a colorant, and a releasing agent is dispersed in an organic solvent in presence of a dispersant, a resultant dispersion liquid is reacted with a cross-linking agent and/or an extender in an aqueous medium, a resultant dispersion liquid is stirred in a stirring tank including a stirrer having a peripheral speed of 5 m/s or more to change a spherical particle to a spindle shape, and then the solvent is removed from the

dispersion liquid. (10) The toner as described in the above item (8) or (9), characterized in that a glass transition point of the polyester resin contained in the toner is 40 to 70 °C.

(11) The toner as described in any one of the above items (8) to 5 (10), characterized in that an acid value of the polyester resin contained in the toner is 1 to 30 mgKOH/g. (12) The toner as described in any one of the above items (1) to (11), characterized in that the toner is used for a two-component developer.

10 Further, the above problems are solved by (13) an image forming apparatus according to the present invention, having a transfer means for transferring a toner image carried on a toner image carrier to a transfer material, and a cleaning means for cleaning toner remaining on a surface of the toner image carrier 15 after the transfer by using a blade, characterized by using the toner as described in any one of above items (1) to (12).

Furthermore, the above problems are solved by (14) a process cartridge according to the present invention which integrally supports a photoconductor, and at least one means selected from a 20 group of a photoconductor, a charge means, a development means, and a cleaning means, and is freely attachable to and detachable from an image forming apparatus body, characterized in that the development means holds toner (developer), and the toner (developer) is dry type toner as described in any one of the 25 above items (1) to (12).

[0012]

That is, according to the present invention, toner and an image forming method described below are provided.

The present invention provides toner and a developer, and an 30 image forming apparatus which are excellent in recycling efficiency based on a two-component developer containing toner of the present invention by using an image forming apparatus of an oilless fixing method having a recycling mechanism for returning

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collected toner from a cleaning part to a developing part.

[0013]

[Description of the Preferred Embodiments]

In the following, an image forming method of the present  
5 invention is described in detail with reference to drawings.

Fig. 1 shows a digital copier as an example of image forming  
apparatus used in the present invention, using a well-known  
electrophotographic system and including a drum-like  
photoconductor (1) in the inside (for example, MF7070  
10 manufactured by Ricoh Co., Ltd.). A charger (2), an exposure  
means (3), a development means (4), a transfer means (5), and a  
cleaning means (6) which carry out an electrophotographic copy  
process are arranged around the photoconductor (1) along a  
rotation direction shown by an arrow (A). The exposure means (3)  
15 forms an electrostatic latent image on the photoconductor (1)  
based on an image signal read by a reading means (8) from a  
document placed on a document placing table (7) on an upper  
surface of the copier. The electrostatic latent image formed on  
the photoconductor (1) is made into a toner image by the  
20 development means (4), and the toner image is electrostatically  
transferred by the transfer means (5) to transfer paper fed by a  
sheet feeding device (9). The transfer paper having the toner  
image is conveyed to a fixing means (10), fixed, and then ejected  
outside.

25 [0014]

Next, behavior of toner used for the image formation step is  
described by using Figs. 1 and 2. The developing device (4) is a  
two-component developing device, and includes a developer formed  
of a carrier and toner in a developing tank (40). When the  
30 developing device (4) forms a toner image, toner of the developer  
is consumed and the ratio (toner concentration) decreases.  
Therefore, to suppress lowering of image density, when electric  
potential  $V_t$  corresponding to toner concentration in the

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developer reaches a predetermined value or higher (that is, toner concentration is a predetermined value or smaller) with respect to electric potential  $V_{ref}$  corresponding to a target value of toner concentration, toner is replenished from a toner hopper (41) to maintain toner concentration in the developer. Toner concentration in the developer is measured by a permeability sensor (42) attached to a lower case of the developing device. The electric potential  $V_{ref}$  corresponding to the target value of toner concentration is set based on a value  $V_{sp}$  of toner image for measurement (P pattern) formed on the photoconductor measured by a photosensor. Toner replenished via a replenishing roller (43) from the toner hopper (41) is stirred with the carrier by a stirring member (44) in the developing device (4), and triboelectrically charged. The developer formed of the carrier and the toner is thrown up on a development roller (46) by a paddle wheel (45), and adheres to the development roller (46) by action of a magnet in the development roller (46). The developer is conveyed by a sleeve on an outer circumference of the development roller, and a surplus portion is scraped off by a development doctor blade (47). Toner in the developer conveyed to a photoconductor side adheres to the photoconductor by action of a development bias in accordance with the electrostatic latent image.

[0015]

Although the toner adhered to the photoconductor (1) by the above development is electrostatically transferred to the transfer paper by the transfer means (5), approximately 10% of toner is not transferred and remains on the photoconductor. Untransferred toner is scraped off from the photoconductor by a cleaning blade (6a) and a brush roller (6b) of the cleaning means (6). To reuse the scraped and recovered toner as recycled toner (T), the recovered toner falls from an eject port (6c) by the self-weight, and is sent to a conveyance pipe formed of a

connected conveyance pipe (13a) in the recycling device (13) and a rotating screw conveyor (13b) in the pipe as shown in Fig. 3. The pipe and the screw are formed of a metal, such as aluminium and stainless steel, or resin. Then, the toner conveyed by the screw is returned to the development means (4) as the recycled toner.

[0016]

On the other hand, since the toner in contact with the photoconductor (1) of the untransferred part or a non-image area adheres also to a transfer belt (5a) of the transfer means (5), the cleaning means (11) is provided on the transfer belt (5a). Residual toner on the transfer belt (5a) is scraped off by a cleaning blade (not illustrated) in slide contact with the belt. Since there is a high possibility that foreign matters, such as paper dust, are contained in the scraped toner, the toner is not recycled in the present example and falls from an eject port by the self-weight, and is sent to waste toner tank (12) as a recovered toner container via a toner guide screw pipe (dotted line).

[0017]

In the present invention, while using an image forming apparatus including a toner recycling mechanism having thus much heat stress and machine stress, a polymer fine particle of the present invention having a specific particle diameter and particle size distribution, and a coated toner particle surface exhibits profound effect to the above stress. Specifically, charging deterioration due to oozing out of wax for releasing agent effect to the particle surface, and charging deterioration due to adhesion of the wax to the carrier are prevented. When the heat stress is applied to the developer, the wax appears on the toner surface, and excessive wax adheres also to the carrier surface. As a result, when toner polarity is negative and wax of same polarity adheres to the carrier, a phenomenon that a charge



amount of the developer deteriorates is caused. Since further low temperature fixation, a high-resolution and high-definition image are required as an aim of recent quality improvement, toner has a smaller diameter, sharper particle size distribution, and lower softening point. Therefore, a surface exposure ratio of wax further increases, which is a disadvantageous situation for toner in the recycling mechanism. The present invention provides toner having a small diameter, sharp particle size distribution, and spherical shape, but cleanability, and excellent storage stability or a toner-release characteristic although Tg of the toner decreases to achieve lower temperature fixation.

[0018]

In the toner of the present invention, high resolution and high quality toner is obtained when a ratio ( $D_v/D_n$ ) of a volume average particle diameter ( $D_v$ ) to a number average particle diameter ( $D_n$ ) is 1.00 to 1.30. In a two-component developer, even after consumption and addition of toner over a long period of time, a variation in the particle diameter of toner in the developer decreases, and satisfactory and stabilized development characteristics are obtained also in long-term stirring in a developing device. When a ratio  $D_v/D_n$  exceeds 1.30, a variation in the particle diameter of individual toner particle is large, a variation in behavior of toner in development or the like is caused, and fine dot reproducibility is spoiled, and a high-definition image is no longer obtained. Still more preferably, a range of  $D_v/D_n$  is 1.00 to 1.20, and thus a more satisfactory image is obtained.

The volume average particle diameter  $D_v$  is preferably 4.0 to 6.0  $\mu\text{m}$ . Generally, the smaller a particle diameter of toner, the more advantageous for obtaining a high-definition and high-resolution image, but conversely disadvantageous for transfer ability or cleanability.

[0019]

When a volume average particle diameter is smaller than the above range, in the two-component developer, toner fuses and adheres to the carrier surface during long-term stirring in a developing device, which yields deterioration of charge ability of the carrier, or easily causes filming of toner to a development roller, or fusion adhering of toner to members, such as a blade for thinning a toner layer when used as a one-component developer. Content of fine powder significantly affects the phenomena. In particular, when particles equal to or smaller than 3  $\mu\text{m}$  exceed 10 %, the particles adhere to the carrier or interfere stability of charge at high levels. In contrast, when a particle diameter of toner is larger than the range, a high quality image with a high resolution is hardly obtained, and the particle diameter of the toner shows a large variation in many cases after consumption and addition of the toner in a developer. Same applies to a case where a ration of volume average particle diameter/number average particle diameter is larger than 1.30.

As mentioned above, since the toner having a small and uniform particle diameter causes difficulty concerning the cleanability and the recycling efficiency, a range of shape factor SF-1 of the toner is preferably 140 to 200.

[0020]

A relationship between a toner shape and transfer ability is described first. When a full-color copier performing transfer in multicolor development is used, an amount of toner on a photoconductor increases as compared with a case of monochrome black toner used for a black and white copier, transfer efficiency is difficultly improved only by using conventional toner with an irregular shape.

From a viewpoint of a balance between blade cleaning and transfer efficiency, compatibility between the cleanability and the transfer ability is achieved when the shape factor SF-1 of

the toner is 140 to 200, preferably 150 to 180. Since the cleanability and the transfer ability significantly depend on a material of a blade and a position of the blade, and transfer also differs depending on a process condition, a design may be achieved in the range of SF-1 in accordance with a process. However, toner with SF-1 less than 140 is difficultly cleaned with a blade. When SF-1 exceeds 200, deterioration of transfer ability mentioned above is seen. In the phenomenon, a toner shape is made irregular, movement of toner in transfer (photoconductor surface to transfer paper, and the like) become less smooth, and variation in behavior is caused between toner particles, whereby uniform and high transfer efficiency is no longer obtained. In addition, instability of charge and fragility of particles develop. Furthermore, a phenomenon of fine powder in a developer occurs, which becomes a factor of deterioration in durability of the developer.

[0021]

Toner has preferably a spindle shape with a shape factor SF-1 in the range of 140 to 200. The spindle shape has a less uneven surface, and excellent transfer ability next to a spherical shape. The spindle shape exhibits a satisfactory cleanability and recycling efficiency which have a trade-off relationship with transfer ability. Therefore, the spindle shape may be considered as a significantly well-balanced shape. In a case of a recycling system, when SF-1 close to a true sphere has satisfactory transfer ability and toner conveyability, but in blade cleaning, a toner cleaning defect occurs, and toner may not be recycled.

Meanwhile, when SF-1 exceeds 200, a shape change and fine powder formation occur during conveyance, and then defective charge or toner deterioration due to agglomeration occurs, which is not preferable.

An optimum shape factor SF-1 in the recycling system is 140 to 200. Since a desolventization step differs from a case of the

present invention, shape control is difficult in conventional suspension polymerization or emulsion polymerization.

[0022]

(Toner shape)

5 In the present invention, SF-1 representing a shape factor of toner is a conventionally known coefficient, and for example, SF-1 may be determined by sampling at random 100 toner images magnified 500 times by using FE-SEM (S-800) manufactured by Hitachi, Ltd., and analyzing image information introduced into an  
10 image analyzing device (Luzex III) manufactured by NIRECO Corporation via an interface.

[0023]

Toner used in a recycling system for particles having average circularity of 2  $\mu\text{m}$  or smaller measured by a flow particle image  
15 analyzing device is required to limit a toner shape and content of particles of 2  $\mu\text{m}$  or smaller measured by the flow particle image analyzer for keeping high quality image and cleanability and recycling efficiency over a long period of time.

Further, for keeping long-term cleanability in repeated use,  
20 and for preventing deterioration of charge ability of a carrier occurring when toner in a two-component developer fuses and adheres to a surface of the carrier in long-term stirring, or for preventing filming of toner to a development roller, and fusion adhering of toner to members, such as a blade for thinning a  
25 toner layer, when used as a one-component developer, an amount of particles of less than 2.0  $\mu\text{m}$  is effectively 15 % or less by number in an equivalent circle diameter of a number basis measured by a flow type particle image analyzer.

Since a Coulter Counter (TA II) measures resistance change in  
30 electric signal, a fine particle of 2  $\mu\text{m}$  or smaller significantly receives influence of noise, and thus the Coulter Counter lacks accuracy of measurement. In contrast, the flow type particle image analyzer which performs measurement based on image

analysis is capable of measuring fine particles of 2  $\mu\text{m}$  or smaller. By reducing content of fine particles (hereinafter, referred to as ultrafine toner) having an equivalent circle diameter of 2  $\mu\text{m}$  or smaller measured by the flow type particle image analyzer, toner adhesion to a conveyance system of toner is found to not occur in repeated use over a long period of time.

When circularity is 0.95 or more, that is, when there are many round particles, slipping of the particles occurs and cleanability may not be maintained over a long period of time in a contact process type cleaning system.

[0024]

The equivalent circle diameter of the flow type particle image used for measurement of the particles in the present invention and percentages by number in each circularity may be measured by using a flow type particle image analyzer FPIA-1000 manufactured by SYSMEX Corporation. Outlines of the analyzer and measurement are described in Japanese Patent Laid-open Publication No. Hei8-136439. The measurement is performed by adding 0.1 to 5 ml of a surfactant as a dispersant, preferably an alkylbenzene sulfonate, to 50 to 100 ml of a 1 % NaCl aqueous solution adjusted by using extra pure (first grade) sodium chloride passed through a filter of 0.45  $\mu\text{m}$ , and then adding 1 to 10 mg of a sample. A resultant suspension is subjected to dispersion treatment for 1 minute by using an ultrasonic dispersion device, and measurement is performed by using a dispersion liquid in which particle concentration is adjusted to 5,000 to 15,000 particles/ $\mu\text{m}$ . Number of particles is calculated by using a diameter of circle having a same area as a two-dimensional image area imaged by a CCD camera as an equivalent circle diameter. Measurement data of the particles was obtained by validating 0.6  $\mu\text{m}$  or more in a equivalent circle diameter based on precision of the pixel of CCD.

[0025]

(Toner particle diameter)

An average particle diameter and particle size distribution of toner are measured by a Coulter counter method. As a measuring device of particle size distribution of the toner particle, a  
5 Coulter Counter TA-II and Coulter Multisizer II (both are manufactured by Beckman Coulter, Inc.) are exemplified.  
In the present invention, number distribution and volume distribution are determined by using the Coulter Counter TA-II connected to a computer PC9801 (manufactured by NEC Corporation)  
10 via an interface (manufactured by The Institute of Japanese Union of Scientists & Engineers).

[0026]

The measurement method is described below.

First, 0.1 to 5 ml of a surfactant (preferably alkylbenzene  
15 sulfonate) is added as a dispersant to 100 to 150 ml of an electrolyte. Here, the electrolyte is an approximately 1 % aqueous solution of NaCl prepared by using an extra pure (first grade) sodium chloride, and ISOTON-II (manufactured by Beckman Coulter, Inc.) may be used, for example. Next, 2 to 20mg of a  
20 test sample to be measured was added. The electrolyte suspending the test sample is subjected to dispersion treatment for approximately 1 to 3 minutes by using an ultrasonic dispersion device, and the volume and the number of toner or toner particles are measured with the measuring device by using an aperture of  
25 100  $\mu\text{m}$  as an aperture to calculate the volume distribution and the number distribution.

[0027]

As channels, 13 channels of 2.00 to less than 2.52  $\mu\text{m}$ ; 2.52 to less than 3.17  $\mu\text{m}$ ; 3.17 to less than 4.00  $\mu\text{m}$ ; 4.00 to less  
30 than 5.04  $\mu\text{m}$ ; 5.04 to 6.35 less than  $\mu\text{m}$ ; 6.35 to less than 8.00  $\mu\text{m}$ ; 8.00 to less than 10.08  $\mu\text{m}$ ; 10.08 to less than 12.70  $\mu\text{m}$ ; 12.70 to less than 16.00  $\mu\text{m}$ ; 16.00 to less than 20.20  $\mu\text{m}$ ; 20.20

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to less than 25.40  $\mu\text{m}$ ; 25.40 to less than 32.00  $\mu\text{m}$ ; 32.00 to less than 40.30  $\mu\text{m}$  were used. The objects were particles having a particle diameter 2.00  $\mu\text{m}$  or more to less than 40.30  $\mu\text{m}$ . A volume average particle diameter ( $D_v$ ) based on the volume determined from the volume distribution of the present invention and a number average particle diameter ( $D_n$ ) determined from the number distribution, and the ratio  $D_v/D_n$  were determined.

[0028]

(Resin fine particle)

10 Resin fine particles used in the present invention have a glass transition point ( $T_g$ ) of 50 to 90  $^{\circ}\text{C}$  as a condition. When a glass transition point ( $T_g$ ) is less than 50  $^{\circ}\text{C}$ , toner storage stability deteriorates and blocking occurs during storage and in a developing device. When a glass transition point ( $T_g$ ) is more  
15 than 90  $^{\circ}\text{C}$ , resin fine particles obstruct adhesiveness with fixing paper, and increase a lowest fixing temperature. A range of 50 to 70  $^{\circ}\text{C}$  is a more preferable range.

A weight average molecular weight is desirably 100,000 or less, preferably 50,000 or less. The lower limit is generally  
20 4,000. When a weight average molecular weight exceeds 100,000, resin fine particles obstruct adhesiveness with fixing paper, and increase a lowest fixing temperature.

[0029]

Publicly known resin may be used as a resin fine particle, as  
25 long as the resin is capable of forming an aqueous dispersion, and either a thermoplastic resin or a thermosetting resin may be used. Examples of such resin include a vinyl resin, a polyurethane resin, an epoxy resin, a polyester resin, a polyamide resin, a polyimide resin, a silicon resin, a phenolic  
30 resin, a melamine resin, a urea resin, an aniline resin, an ionomer resin, a polycarbonate resin, and the like. As resin fine particles, two or more kinds of above resins may be used in

combination. Among the resins, the vinyl resin, the polyurethane resin, the epoxy resin, the polyester resin, or resins in combination thereof is preferable from a viewpoint that an aqueous dispersion of fine spherical resin particles is easily obtained.

5 [0030]

The vinyl resin is a polymer obtained by homopolymerizing or copolymerizing a vinyl monomer, and includes for example, a styrene-(meth)acrylic ester resin, a styrene-butadiene copolymer, a (meth)acrylic acid-acrylic ester polymer, a  
10 styrene-acrylonitrile copolymer, a styrene-maleic anhydride copolymer, a styrene-(meth)acrylic acid copolymer, and the like. In the resin fine particle, the average particle diameter is 5 to 200 nm, preferably 20 to 300 nm.

[0031]

15 (Hot offset characteristic)

Relating to hot offset resistance, various investigations have been made for controlling molecular weight distribution of a binder resin. To combine opposite properties of a low temperature fixing property and hot offset resistance, for example, a binder  
20 resin with wide molecular weight distribution is used, or resin having at least two molecular weight peaks of a polymer component with a molecular weight of several hundreds of thousands to several millions and a low molecular component with a molecular weight of thousands to tens of thousands, is mixed, and a  
25 function of each component is separated. The polymer component is more effective for hot offset when the polymer component has a cross-linking structure or is in a state of a gel.

[0032]

Molecular weight distribution of a binder component (resin  
30 component) in toner is measured by a method shown below.

Approximately 1 g of toner is precisely weighed in an Erlenmeyer flask, 10 to 20 g of THF (tetrahydrofuran) is added to obtain a THF solution of 5 to 10 % binder concentration. A column



is stabilized in a heat chamber at 40 °C, THF is fed in the column at the temperature at a flow rate of 1 ml/min as a solvent, and 20  $\mu$ l of the above THF sample solution is injected into the column. A molecular weight of the test sample was calculated from a relationship of a logarithm of a calibration curve prepared by using monodisperse polystyrene standard samples and retention time. The calibration curve was prepared by using the polystyrene standard samples. As the monodisperse polystyrene standard samples, monodisperse polystyrene (manufactured by Tosoh Corporation) having a molecular weight of  $2.7 \times 10^2$  to  $6.2 \times 10^6$  is used, for example. A refractive index (RI) detector is used as a detector. As the column, a combination of columns, for example TSK gel, G 1000H, G 2000H, G 2500H, G 3000H, G 4000H, G 5000H, G 6000H, G 7000H, and GMH manufactured by Tosoh Corporation is used.

A THF-soluble resin component has a main peak molecular weight (Mp) of generally 2,500 to 10,000, preferably 2,000 to 8,000. When an amount of component having a molecular weight less than 2,500 increases, heat-resistant storage stability tends to deteriorate, and when a component having a molecular weight exceeding 10,000 increases, a low temperature fixing property tends to deteriorate, but the deterioration may be suppressed by balance control. Content of a component having a molecular weight exceeding 10,000 is 1 % to 10 %, preferably 3 to 6 % although depending on a toner material. Sufficient hot offset resistance is not obtained at less than 1 %, but at 10 % or more, glossiness and transparency deteriorate. Content of a component having a molecular weight less than 2,500 is 0.1 to 5.0 %.

A number average molecular weight (Mn) of the THF-soluble resin component is 2,000 to 15,000, and a ratio Mw/Mn (Mw: weight average molecular weight) is preferably 5 or less. When the ratio is 5 or more, a sharp melt property lacks and glossiness is spoiled. Moreover, use of a polyester resin containing 1 to 25 % of a THF-insoluble component leads to improvement in hot offset.

[0033]

(Binder resin)

Conventional common materials may be used as a binder resin. Conventionally, the binder resin used for toner production includes a polyester resin, a styrene resin, an acrylic resin, an epoxy resin, for example. However, in common toner, resin formed of a copolymer of styrene and an acrylic ester is most generally used. On the other hand, in low temperature fixing toner, resin having a tendency to easily satisfy the heat characteristic mentioned above is used. The polyester resin has a low softening temperature and a high glass transition point as the binder resin, and is excellent in the low temperature fixing property and the storage stability. Further since the polyester resin has satisfactory affinity of an ester bond with paper, toner excellent also in offset resistance is obtained.

[0034]

The polyester resin used as a main component of the binder resin of toner for electrostatic charge image development according to the present invention is compounded by a condensation reaction of an acid component and an alcohol component, or a ring breakage reaction of a cyclic ester, or compounded by a reaction of a halogenated compound, an alcohol component, and carbon monoxide. In a method of manufacturing toner for electrostatic charge image development of the present invention, the above monomers serving as synthetic materials of the polyester resin are combined and polymerized in the (above) high molecular compound solution, thereby easily obtaining the toner for electrostatic charge image development of the present invention having excellent physical properties described previously. In the following, various monomers used as synthetic materials of the polyester resin are described.

[0035]

Divalent or higher-valence compounds are preferably used as

the alcohol component and the acid component. Examples of dihydric alcohols are: ethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, and other diols; bisphenol A, hydrogenated bisphenol A,  $\alpha, \alpha'$ -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene, polyoxyethylenated bisphenol A, polyoxypropylenated bisphenol A, and other alkylene oxide adducts of bisphenol A.

[0036]

10 Examples of trihydric or higher alcohols include, for example, sorbitol, 1,2,3,6-hexanetetrol, 1,4-sorbitan, pentaerythritol, sucrose, 1,2,4-butanetriol, 1,2,5-pentanetriol, glycerol, 2-methylpropanetriol, 2-methyl-1,2,4-butaneditriol, trimethylolmethane, trimethylolethane, trimethylolpropane, and  
15 1,3,5-trihydroxymethylbenzene.

[0037]

Examples of dibasic acids are maleic acid, fumaric acid, citraconic acid, itaconic acid, glutaconic acid, phthalic acid, isophthalic acid, terephthalic acid, cyclohexanedicarboxylic acid, succinic acid, adipic acid, sebacic acid, azelaic acid, malonic  
20 acid, and other dibasic organic acids. Examples of tribasic or higher acids are 1,2,4-benzenetricarboxylic acid, 1,2,5-benzenetricarboxylic acid, 1,2,4-cyclohexanetricarboxylic acid, 2,5,7-naphthalenetricarboxylic acid, 1,2,5-naphthalenetricarboxylic acid, 1,2,5-hexanetricarboxylic  
25 acid, 1,3-dicarboxyl-2-methyl-2-carboxymethylpropane, tetrakis(carboxymethyl)methane, and 1,2,7,8-octanetetracarboxylic acid. Acid anhydrides and acid halides of the organic acids are also preferably used as the acid component.

30 [0038]

Halogen compounds may be used as a compound corresponding to the acid component. Examples of the halogen compounds are compounds each having two or more halogen atoms, such as

cis-1,2-dichloroethene, trans-1,2-dichloroethene,  
1,2-dichloropropene, 2,3-dichloropropene, 1,3-dichloropropene,  
o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene,  
o-dibromobenzene, m-dibromobenzene, p-dibromobenzene,  
5 o-chlorobromobenzene, dichlorocyclohexane, dichloroethane,  
1,4-dichlorobutane, 1,8-dichlorooctane, 1,7-dichlorooctane,  
dichloromethane, 4,4'-dibromovinylphenol, and  
1,2,4-tribromobenzene.

[0039]

10 As a synthesis component of polyester resin, a compound  
having an aromatic ring is preferably used for either one of the  
acid component and the alcohol component. Moreover, in the  
present invention, the total amount of the acid component and  
alcohol component which are the synthesis components of the  
15 polyester resin preferably ranges from 1 to 30 parts, preferably  
1.5 parts to 10 parts to 1 part of the polymer compound described  
earlier.

A use ratio of the acid component to the alcohol component is  
such that the amount of alcohol groups is preferably in a range  
20 of from 0.9 to 1.5 mole equivalent, and more preferably from 1.0  
to 1.3 mole equivalent relative to 1 mole equivalent of carboxyl  
groups. The term "carboxyl group" as used herein also includes  
the halogen compounds corresponding to the above-mentioned acid  
component. As other additives, an amine component may be used,  
25 such as triethylamine, trimethylamine, and N,N-dimethylaniline.  
Other condensing agents such as dicyclohexylcarbodiimide may also  
be used in the reaction.

[0040]

(Modified polyester reactive with active hydrogen group)

30 Reactive modified polyester resin reactive with an active  
hydrogen group (RMPE) (hereinafter the polyester resin may be  
simply referred to as "polyester") includes, for example,  
polyester prepolymers having a functional group reactive with an

active hydrogen group such as an isocyanate group. An isocyanate-containing polyester prepolymer (A) is suitably used as a polyester prepolymer in the present invention. The isocyanate-containing polyester prepolymer (A) is prepared by  
5 allowing a polyester being a polycondensate of a polyol (PO) and a polycarboxylic acid (PC) and having an active hydrogen group to react with a polyisocyanate compound (PIC). The active hydrogen group of the polyester includes, for example, hydroxyl groups (alcoholic hydroxyl groups and phenolic hydroxyl groups), amino  
10 groups, carboxyl groups, and mercapto groups, of which the alcoholic hydroxyl groups are preferred.

[0041]

Examples of the polyol include diols (DIO) and trihydric or higher polyols (TO). As the polyol, a diol (DIO) alone or a  
15 mixture of a diol (DIO) and a small amount of a polyol (TO) is preferred. Examples of the diol include alkylene glycols (ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,6-hexanediol, and the like); alkylene ether glycols (diethylene glycol, triethylene glycol, dipropylene  
20 glycol, polyethylene glycol, polypropylene glycol, polytetramethylene ether glycol, and the like); alicyclic diols (1,4-cyclohexanedimethanol, hydrogenated bisphenol A, and the like); bisphenols (bisphenol A, bisphenol F, bisphenol S, and the like); alkylene oxide (ethylene oxide, propylene oxide, butylene  
25 oxide, and the like) adducts of the aforementioned alicyclic diols; and alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, and the like) adducts of the aforementioned bisphenols. Among the compounds, alkylene glycols having 2 to 12 carbon atoms, and alkylene oxide adducts of bisphenols are  
30 preferred, of which the alkylene oxide adducts of bisphenols alone or in combination with any of the alkylene glycols having 2 to 12 carbon atoms are particularly preferred.

The trihydric or higher polyols include, for example,

trihydric, octahydric or higher aliphatic alcohols (glycerol, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, and the like); trihydric or higher phenols (trisphenol PA, phenol novolacs, cresol novolacs, and the like); and alkylene oxide  
5 adducts of the above trihydric or higher polyphenols.

[0042]

Examples of the polycarboxylic acid (PC) include, for example, dicarboxylic acids (DIC) and tri- or higher polycarboxylic acids (TC). As the polycarboxylic acid (PC), a dicarboxylic acid (DIC)  
10 alone or in combination with a small amount of a tri- or higher polycarboxylic acid (TC) is preferred.

Examples of the dicarboxylic acids include alkylenedicarboxylic acids (succinic acid, adipic acid, and sebacic acid, and the like); alkenylenedicarboxylic acids (maleic  
15 acid, and fumaric acid); aromatic dicarboxylic acids (phthalic acid, isophthalic acid, terephthalic acid, and naphthalenedicarboxylic acid, and the like). Among the mentioned compounds, preferred are alkenylenedicarboxylic acids each having  
20 4 to 20 carbon atoms and aromatic dicarboxylic acids each having 8 to 20 carbon atoms.

The tri- or higher polycarboxylic acids include, for example, aromatic polycarboxylic acids each having 9 to 20 carbon atoms (trimellitic acid and pyromellitic acid, and the like). A  
25 polycarboxylic acid may be obtained by bringing the acid anhydride or lower alkyl ester (methyl ester, ethyl ester, and propyl ester, and the like) of the above polycarboxylic acids  
into reaction with a polyol.

The ratio of the polyol to the polycarboxylic acid is, in terms of an equivalent ratio  $[OH]/[COOH]$  of the hydroxyl group  
30  $[OH]$  and the carboxyl group  $[COOH]$ , generally chosen to be 2/1 to 1/1, preferably 1.5/1 to 1/1, and more preferably 1.3/1 to 1.02/1.

[0043]

Examples of the polyisocyanate (PIC) include aliphatic

polyisocyanates (tetramethylene diisocyanate, hexamethylene diisocyanate, 2,6-diisocyanatomethyl caproate, and the like); alicyclic polyisocyanates (isophorone diisocyanate, cyclohexylmethane diisocyanate, and the like); aromatic diisocyanates (tolylene diisocyanate, diphenylmethane diisocyanate, and the like); aromatic-aliphatic diisocyanates such as  $\alpha, \alpha, \alpha', \alpha'$ -tetramethylxylylene diisocyanate; isocyanurates; the polyisocyanates blocked, for example, with phenol derivatives, oximes, or caprolactams; and mixtures of the above compounds.

The ratio of the polyisocyanate ranges, in terms of an equivalent ratio  $[NCO]/[OH]$  of the isocyanate group  $[NCO]$  to the hydroxyl group  $[OH]$  of the hydroxyl-containing polyester, generally from 5/1 to 1/1, preferably from 4/1 to 1.2/1, and more preferably from 2.5/1 to 1.5/1. If the ratio  $[NCO]/[OH]$  exceeds 5, image-fixing properties at low temperatures deteriorates. If the ratio  $[NCO]/[OH]$  is smaller than 1, a urea content in the modified polyester decreases, and hot offset resistance deteriorates. The content of the polyisocyanate (PIC) component in the prepolymer (A) having an isocyanate group at the end ranges generally from 0.5 % to 40 % by weight, preferably from 1 % to 30 % by weight, and more preferably from 2 % to 20 % by weight. If the content is smaller than 0.5 % by weight, the hot offset resistance deteriorates, and satisfactory storage stability at high temperatures and image-fixing properties at low temperatures may not be obtained concurrently. On the other hand, if the content exceeds 40 % by weight, the image-fixing properties at low temperatures deteriorate.

[0044]

The isocyanate-containing polyester prepolymer (A) generally has, in average, 1 or more, preferably 1.5 to 3, and more preferably 1.8 to 2.5 isocyanate groups per molecule. If the number of the isocyanate group per molecule is smaller than 1, a

resulting urea-modified polyester may have a low molecular weight and the hot offset resistance deteriorates.

By allowing the isocyanate-containing polyester prepolymer (A) to react with an amine (B), a urea-modified polyester (UMPE) may be prepared. The resultant urea-modified polyester (UMPE) demonstrates superior effects as a toner binder.

[0045]

The amine (B) includes, for example, diamines (B1), tri- or higher polyamines (B2), amino alcohols (B3), aminomercaptans (B4), amino acids (B5), and amino-blocked products (B6) in which the amino groups of the amines (B1) to (B5) are blocked. The diamines (B1) include aromatic diamines (phenylenediamine, diethyltoluenediamine, 4,4'-diaminodiphenylmethane, and the like); alicyclic diamines (4,4'-diamino-3,3'-dimethyldicyclohexylmethane, diaminocyclohexanes, isophoronediamine, and the like); and aliphatic diamines (ethylenediamine, tetramethylenediamine, hexamethylenediamine, and the like). The tri- or higher polyamines (B2) include, diethylenetriamine, triethylenetetramine, and the like. The amino alcohols (B3) include ethanolamine, hydroxyethylaniline, and the like. The aminomercaptans (B4) include aminoethyl mercaptan, aminopropyl mercaptan, and the like. The amino acids (B5) include aminopropionic acid, aminocaproic acid, and the like. The amino-blocked products (B6) in which the amino groups of the amines (B1) to (B5) are blocked include ketimine compounds and oxazolidine compounds derived from the amines (B1) to (B5) and ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, and the like). Among the above amines (B), preferred are (B1) alone and in combination with a small amount of B2.

[0046]

Where necessary, the molecular weight of the modified polyester may be controlled by using an extension terminator.



Such extension terminators include monoamines (diethylamine, dibutylamine, butylamine, laurylamine, and the like); and blocked products thereof (ketimine compounds).

[0047]

5       The content of the amine (B) in terms of the equivalent ratio  $[\text{NCO}]/[\text{NH}_x]$  of isocyanate groups  $[\text{NCO}]$  in the prepolymer (A) having isocyanate groups to amino groups  $[\text{NH}_x]$  of the amines (B) is generally in the range of from 1/2 to 2/1, preferably from 1.5/1 to 1/1.5 and more preferably from 1.2/1 to 1/1.2. If the  
10       ratio  $[\text{NCO}]/[\text{NH}_x]$  exceeds 2 or is smaller than 1/2, the urea-modified polyester may have a low molecular weight, and the hot offset resistance may deteriorate. The urea bond-modified polyester of the present invention may include a urethane bond in  
15       addition to the urea bond. The molar ratio of the content of the urea bond to the content of the urethane bond is generally in the range of from 100/0 to 10/90, preferably from 80/20 to 20/80, and more preferably from 60/40 to 30/70. If the molar ratio of the urea bond is smaller than 10 %, the hot offset resistance deteriorates.

20       The amines (B) serve as a crosslinking agent or an extender for the modified polyester which is capable of reacting with active hydrogen.

[0048]

25       The urea-modified polyester for use in the present invention is produced, for example, by a one-shot method or a prepolymer method. The weight-average molecular weight of the modified polyester such as the urea-modified polyester ranges generally 10,000 or more, preferably from 20,000 to 10 million and more preferably from 30,000 to 1 million. If the weight-average  
30       molecular weight is smaller than 10,000, the hot offset resistance may deteriorate. The number-average molecular weight of the modified polyester, such as the urea-modified polyester, is not specifically limited when an unmodified polyester to be

mentioned later is used, and may be such a number-average molecular weight as to easily yield the above-specified weight-average molecular weight. If the modified polyester is used alone, the number-average molecular weight thereof ranges generally 20,000 or smaller, preferably from 1,000 to 10,000, and more preferably from 2,000 to 8,000. If the number-average molecular weight exceeds 20,000, the image-fixing properties at low temperatures and glossiness upon use in a full-color apparatus deteriorate.

10 [0049]

(Unmodified polyester)

In the present invention, the modified polyester (MPE) may be used alone or in combination with an unmodified polyester (PE) as a toner binder component. By using the PE in combination, the image-fixing properties at low temperatures and glossiness upon use in a full-color apparatus are improved, and a more preferable result is obtained than when the modified polyester is used alone. The examples of the PE include polycondensation products of a polyol and a polycarboxylic acid as in the polyester component of the MPE, and preferred substances are identical to the examples of the MPE. The PE may include not only unmodified polyesters but also polyesters modified with another chemical bond other than the urea bond, and may be modified with the urethane bond. The MPE and the PE are preferably at least partially compatible with each other for better image-fixing properties at low temperatures and hot-offset resistance. Accordingly, the MPE preferably has a polyester component similar to the polyester component of the PE. The weight ratio of the MPE to the PE, when the PE is included, ranges generally from 5/95 to 80/20, preferably from 5/95 to 30/70, more preferably from 5/95 to 25/75, and particularly preferably from 7/93 to 20/80. If the weight ratio is smaller than 5 %, hot offset resistance may deteriorate, and satisfactory storage stability at high temperatures and image fixing

properties at low temperatures may not be obtained concurrently.

[0050]

The peak molecular weight of the PE ranges generally from 1,000 to 30,000, preferably from 1,500 to 10,000, and more preferably from 2,000 to 8,000. If the peak molecular weight is smaller than 1,000, the storage stability at high temperatures deteriorates, if the peak molecular weight exceeds 30,000, the image-fixing properties at low temperatures deteriorates considerably, and if the peak molecular weight exceeds 10,000, the image-fixing properties at low temperatures deteriorates slightly. The hydroxyl value of the PE ranges preferably 5 or more, more preferably from 10 to 120, and particularly preferably from 20 to 80. If the hydroxyl value is smaller than 5, satisfactory storage stability at high temperatures and image-fixing properties at low temperatures may not be obtained concurrently. The acid value of the PE ranges generally from 1 to 30, and preferably from 5 to 20. A binder having such an acid value tends to be negatively charged.

[0051]

The glass transition point ( $T_g$ ) of the binder in the toner (toner binder) for use in the present invention ranges generally from 50 to 70 °C, and preferably from 55 to 65 °C. If the glass transition point is lower than 50 °C, the heat storage stability of the toner may deteriorate. If the glass transition point exceeds 70 °C, the image-fixing properties at low temperatures may be insufficient. By coexistence of the modified polyester resin, such as urea-modified polyester resin, the dry toner according to the present invention shows, even with a lower glass transition point, higher heat storage stability than conventional polyester toners. The storage elastic modulus of the toner binder is such that a temperature  $TG'$  at which the storage elastic modulus measured at 20 Hz is 10,000 dyne/cm<sup>2</sup> ranges generally 100 °C or higher, and preferably from 110 °C to 200 °C. If the

temperature TG' is lower than 100 °C, hot offset resistance deteriorates. A temperature ( $T_{\eta}$ ) at which the viscosity of the toner binder is 1,000 poises as determined at 20 Hz is generally 180 °C or lower, and preferably in the range of from 90 °C to 160 °C. If the temperature  $T_{\eta}$  exceeds 180 °C, the image-fixing properties at low temperatures deteriorate. To obtain satisfactory image-fixing properties at low temperatures and hot offset resistance concurrently, TG' is preferably higher than  $T_{\eta}$ . In other words, the difference between TG' and  $T_{\eta}$  ( $TG' - T_{\eta}$ ) is preferably 0 °C or more, more preferably 10 °C or more, and particularly preferably 20 °C or more. The upper limit of the difference is not limited. To obtain satisfactory heat storage stability and image-fixing properties at low temperatures concurrently, the difference between  $T_{\eta}$  and  $T_g$  is preferably in the range of from 0 to 100 °C, more preferably from 10 to 90 °C, and particularly preferably from 20 to 80 °C.

[0052]

(Colorant)

Any conventional or known dye and pigments may be used as the colorant of the present invention. Such dyes and pigments include carbon black, nigrosine dyes, black iron oxide, Naphthol Yellow S, Hansa Yellow (10G, 5G, and G), cadmium yellow, yellow iron oxide, yellow ocher, chrome yellow, Titan Yellow, Polyazo Yellow, Oil Yellow, Hansa Yellow (GR, A, RN, and R), Pigment Yellow 1, Benzidine Yellow (G, GR), Permanent Yellow (NCG), Vulcan Fast Yellow (5G, R), Tartrazine Lake, Quinoline Yellow Lake, Anthraren Yellow BGL, isoindolinone yellow, colcothar, red lead oxide, red lead oxide, cadmium red, cadmium mercury red, antimony red, Permanent Red 4R, Para red, Fire Red, p-chloro-o-nitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Red (F2R, F4R, FRL, FRLl, F4RH), Fast Scarlet VD, Vulcan Fast Rubine B, Brilliant Scarlet G, Lithol Rubine GX,

Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B,  
Bordeaux 5B, Toluidine Maroon, Permanent Bordeaux F2K, Helio  
Bordeaux BL, Bordeaux 10B, BON Maroon Light, BON Maroon Medium,  
eosine lake, Rhodamine Lake B, Rhodamine Lake Y, Alizarine Lake,  
5 Thioindigo Red B, Thioindigo Maroon, Oil Red, quinacridone red,  
Pyrazolone Red, Polyazo Red, Chrome Vermilion, Benzidine Orange,  
Perynone Orange, Oil Orange, cobalt blue, cerulean blue, Alkali  
Blue Lake, Peacock Blue Lake, Victoria Blue Lake, metal-free  
phthalocyanine blue, Phthalocyanine Blue, Fast Sky Blue,  
10 Indanthrene Blue (RS, BC), indigo, ultramarine, Prussian blue,  
Anthraquinone Blue, Fast Violet B, Methyl Violet Lake, cobalt  
violet, manganese violet, dioxazine violet, Anthraquinone Violet,  
chrome green, zinc green, chromium oxide, viridian, emerald green,  
Pigment Green B, Naphthol Green B, Green Gold, Acid Green Lake,  
15 Malachite Green Lake, Phthalocyanine Green, Anthraquinone Green,  
titanium oxide, zinc white, and lithopone, and mixtures thereof.  
The content of the colorant ranges generally from 1 % by weight  
to 15 % by weight, and preferably from 3 % by weight to 10 % by  
weight of the toner.

20 [0053]

The colorant mentioned in the present invention may be used  
as a master batch compounded with resin. Examples of binder resin  
for use in the production of the master batch or in kneading with  
the master batch are, in addition to the aforementioned modified  
25 and unmodified polyester resin, polymers of styrenes such as  
polystyrene, poly-p-chlorostyrene, polyvinyltoluene, and  
substituted styrenes; styrenic copolymers such as  
styrene-p-chlorostyrene copolymers, styrene-propylene copolymers,  
styrene-vinyltoluene copolymers, styrene-vinylnaphthalene  
30 copolymers, styrene-methyl acrylate copolymers, styrene-ethyl  
acrylate copolymers, styrene-butyl acrylate copolymers,  
styrene-octyl acrylate copolymers, styrene-methyl methacrylate  
copolymers, styrene-ethyl methacrylate copolymers, styrene-butyl

methacrylate copolymers, styrene- $\alpha$ -methyl-chloromethacrylate copolymers, styrene-acrylonitrile copolymers, styrene-vinyl methyl ketone copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, styrene-acrylonitrile-indene copolymers, styrene-maleic acid copolymers, and styrene-maleic ester copolymers; polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, polyvinyl acetate, polyethylene, polypropylene, polyesters, epoxy resin, epoxy polyol resin, polyurethane, polyamides, polyvinyl butyral, polyacrylic resin, rosin, modified rosin, terpene resin, aliphatic or alicyclic hydrocarbon resin, aromatic petroleum resin, chlorinated paraffin, and paraffin wax. Each of the above substances may be used alone or in combination.

[0054]

The master batch may be prepared by mixing and kneading the master batch resin and the colorant under high shearing force. In this process, an organic solvent may be used for enhancing interaction between the colorant and the resin. In addition, a "flushing process" is preferably employed, in which an aqueous paste containing the colorant and water is mixed and kneaded with an organic solvent to thereby transfer the colorant to the resin component, and the water and organic solvent are then removed. According to the present process, a wet cake of the colorant may be used as it is without drying, which makes the process simple and preferable. A high-shear dispersing apparatus such as a three-roll mill may preferably be used in mixing and kneading.

[0055]

(Releasing agent)

A known or conventional releasing agent may be used in the present invention. Such releasing agents include polyolefin wax (polyethylene wax, polypropylene wax, and the like); long-chain hydrocarbons (paraffin wax, Sasol wax, and the like); and carbonyl-containing wax. Preferred wax is carbonyl-containing wax.

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Such carbonyl-containing wax includes, for example, polyalkanoic acid esters (carnauba wax, montan wax, trimethylolpropane tribehenate, pentaerythritol tetrabehehenate, pentaerythritol diacetate dibehenate, glycerol tribehenate, 1,18-octadecanediol distearate, and the like); polyalkanol esters (tristearyl trimellitate, distearyl maleate, and the like); polyalkanoic acid amides (ethylenediaminedibehenylamide, and the like); polyalkylamides (tristearylamide trimellitate, and the like); and dialkyl ketones (distearyl ketone, and the like). Among the carbonyl-containing wax, the polyalkanoic acid esters are preferred. The wax of the present invention generally has a melting point ranging from 40 °C to 160 °C, preferably from 50 °C to 120 °C, and more preferably from 60 °C to 90 °C. Wax with a melting point of lower than 40 °C may adversely affect the storage stability at high temperatures. In contrast, wax with a melting point exceeding 160 °C may often invite cold offset upon image fixing at low temperatures. The wax has a melt viscosity of preferably from 5 to 1,000 cps, and more preferably from 10 to 100 cps as measured at a temperature 20 °C higher than the melting point. Wax with a melt viscosity exceeding 1,000 cps may not satisfactorily contribute to improve hot offset resistance and image-fixing properties at low temperatures. The content of the wax in the toner ranges generally from 0 % to 40 % by weight, and preferably from 3 % to 30 % by weight.

[0056]

(Charge control agent)

The toner may further comprise a charge control agent according to necessity. Charge control agents include known charge control agents such as nigrosine dye, triphenylmethane dye, chromium-containing metal complex dye, molybdic acid chelate pigments, rhodamine dye, alkoxyamines, quaternary ammonium salts (including fluorine-modified quaternary ammonium salts), alkylamides, elementary phosphorus or phosphorus compounds,

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elementary tungsten or tungsten compounds, fluorine-containing active agents, metal salts of salicylic acid, and metal salts of salicylic acid derivatives. Examples of the charge control agents include BONTRON 03 (Nigrosine dyes), BONTRON P-51 (quaternary ammonium salt), BONTRON S-34 (metal-containing azo dye), E-82 (metal complex of oxynaphthoic acid), BONTRON E-84 (metal complex of salicylic acid), and BONTRON E-89 (phenolic condensation product) available from Orient Chemical Industries, Ltd; TP-302 and TP-415 (molybdenum complex of quaternary ammonium salt) available from Hodogaya Chemical Co., Ltd.; COPY CHARGE PSY VP2038 (quaternary ammonium salt), COPY BLUE PR (triphenylmethane derivative), COPY CHARGE NEGVP2036 and COPY CHARGE NX VP434 (quaternary ammonium salt) available from Hoechst AG; LRA-901, and LR-147 (boron complex) available from Japan Carlit Co., Ltd.; as well as copper phthalocyanine pigments, perylene pigments, quinacridone pigments, azo pigments, and polymeric compounds having a functional group such as a sulfonic group, carboxyl group, and quaternary ammonium salt.

[0057]

In the present invention, the amount of the charge control agent is not specifically limited, but is to be determined depending on the type of the binder resin, presence or absence of additives used according to necessity, and a method for preparing the toner including a dispersing process. The amount is preferably in a range of from 0.1 to 10 parts by weight, and more preferably from 0.2 to 5 parts by weight relative to 100 parts by weight of the binder resin. If the amount exceeds 10 parts by weight, the toner may have an excessively high chargeability, the effect of the principal charge control agent may be reduced, the toner may be attracted stronger electrostatically to a development roller, and the fluidity of the developer may be decreased or image density may be reduced. The charge control agent may be melted and kneaded together with the master batch



and resin and then melted and dispersed therein, may of course be added directly to the organic solvent during the melting and dispersion procedures, or may be fixed on the toner surface after toner particle preparation.

5 [0058]

(External additive)

Inorganic fine particles may be preferably used as an external additive to assist the fluidity, development properties and chargeability of the colored resin particles obtained in the present invention. The inorganic fine particles have a primary  
10 particle diameter ranging preferably from 5  $\mu\text{m}$  to 2  $\mu\text{m}$ , more preferably from 5  $\mu\text{m}$  to 500  $\mu\text{m}$ . and have a specific surface area as determined by the BET method ranging preferably from 20 to 500  $\text{m}^2/\text{g}$ . The amount of the employed inorganic fine particles is  
15 preferably in the range of from 0.01 to 5 % by weight, and more preferably from 0.01 to 2.0 % by weight of the toner. Examples of the inorganic fine particles include silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, silica sand, clay,  
20 mica, wollastonite, diatomaceous earth, chromium oxide, cerium oxide, colcothar, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, and silicon nitride.

Other examples of the external additive include polymer fine  
25 particles such as polymer particles obtained by soap-free emulsion polymerization, suspension polymerization or dispersion polymerization from polystyrene or copolymers of methacrylic esters and acrylic esters, polymerization condensation systems such as silicone, benzoguanamine and nylon, and thermosetting  
30 resin.

[0059]

The external additives are surface-treated to improve hydrophobic properties so that fluidity and chargeability are not

impaired even in a high humidity atmosphere. Suitable surface treatment agents are, for example, a silane coupling agent, a sililating agent, a silane coupling agent having a fluorinated alkyl group, an organic titanate-based coupling agent, an  
5 aluminium-based coupling agent, silicone oil, and modified silicone oil. A cleaning property improver may also be added in order to remove the developer remaining on a photoconductor or on a primary transfer material after the transfer.

Suitable cleaning property improvers are, for example, metal  
10 salts of stearic acid and other fatty acids such as zinc stearate, and calcium stearate; and polymer fine particles prepared, for example, by soap-free emulsion polymerization, such as polymethyl methacrylate fine particles, polystyrene fine particles. Such  
15 polymer fine particles preferably have a relatively narrow particle distribution and a volume-average particle diameter of 0.01 to 1  $\mu\text{m}$ .

[0060]

(Method of preparing binder component)

A toner binder may be prepared, for example, by the following  
20 method. A polyol and a polycarboxylic acid are heated at a temperature range of from 150 °C to 280 °C in the presence of a known esterification catalyst such as tetrabutoxy titanate or dibutyltin oxide, and produced water is removed by distillation where necessary under a reduced pressure to thereby obtain a  
25 hydroxyl-containing polyester. The resultant hydroxyl-containing polyester is allowed to react with a polyisocyanate in a temperature range of 40 to 140 °C to thereby obtain an isocyanate-containing prepolymer (A). The prepolymer (A) is  
30 allowed to react with an amine (B) at 0 to 140 °C, and thereby yields a polyester modified with urea bonds. In the reaction with the polyisocyanate and the reaction between A and B, solvents may be used according to necessity. Examples of applicable solvents should be inert to the polyisocyanate (PIC), and include aromatic

solvents (toluene and xylene, and the like); ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, and the like); esters (ethyl acetate, and the like); amides (dimethylformamide and dimethylacetamide, and the like); and ethers (tetrahydrofuran, and the like). When a polyester (PE) not modified with urea bonds is used in combination, the PE is prepared in the same manner as the hydroxyl-containing polyester is produced, and the prepared PE is dissolved in and mixed with a solution of the urea-modified polyester after completion of the reaction.

10 [0061]

(Toner production)

The toner of the present invention may be prepared by the following methods, but other methods may also be possible.

[0062]

15 (Toner Production in aqueous medium)

Aqueous media may include water alone or may be in combination with an organic solvent miscible with water. Such miscible organic solvents include alcohols (methanol, isopropanol, ethylene glycol, and the like); dimethylformamide; tetrahydrofuran; Cellosolves (methyl Cellosolve, and the like); and lower ketones (acetone, methyl ethyl ketone, and the like).

The toner particles may be prepared by allowing a dispersion containing the isocyanate-containing prepolymer (A) to react with amines (B) in the aqueous medium. In an example of the method of forming a dispersion formed of the urea-modified polyester or the prepolymer (A), the dispersion is obtained by adding a composition of toner materials formed of the urea-modified polyester or the prepolymer (A) and dispersing the material into a state of fine particles by applying shear force. Other toner components (hereinafter referred to as "toner materials") such as a colorant, colorant master batch, releasing agent, charge control agent, and unmodified polyester resin may be mixed with the prepolymer (A) when the dispersion is formed in the aqueous

medium. However, more preferably, the toner materials are mixed with one another beforehand and the resulting mixture is added to the aqueous medium. The other toner materials such as the colorant, the releasing agent, and the charge control agent are not necessarily added during particle formation in the aqueous medium, and may be added after particle formation. For example, particles containing no colorant may be first formed, and the colorant may then be added to the formed particles according to a known dying procedure.

10 [0063]

A method of dispersion is not specifically limited, and may include known methods relying, for example, on low-speed shearing, high-speed shearing, friction, high-pressure jetting, and ultrasonic wave facilities. To make an average particle diameter of the dispersion to be 2 to 20  $\mu\text{m}$ , the high-speed shearing method is preferred. When a high-speed shearing dispersing machine is used, the number of rotation is not specifically limited and ranges generally from 1,000 to 30,000 rpm and preferably from 5,000 to 20,000 rpm. Dispersion time is not specifically limited and ranges generally from 0.1 to 5 minutes in a batch system. Dispersion temperature ranges generally from 0 to 150 °C (under pressure) and preferably from 40 to 98 °C. The dispersion is preferably performed at high temperatures for lower viscosity of the dispersion containing the urea-modified polyester or the prepolymer (A) and for easier dispersion.

25 [0064]

The amount of the aqueous medium to be used ranges generally from 50 to 2,000 parts by weight, and preferably from 100 to 1,000 parts by weight relative to 100 parts by weight of the toner composition (composition material) containing the urea-modified polyester or the prepolymer (A). If the amount is smaller than 50 parts by weight, the toner composition may not be dispersed sufficiently to thereby fail to yield toner

particles having a predetermined average particle diameter. If the amount exceeds 2,000 parts by weight, the manufacturing processing becomes uneconomical. Where necessary, a dispersing agent may be used. Such a dispersing agent is preferably used for sharper particle distribution and stabler dispersion.

The urea-modified polyester may be synthesized from the prepolymer (A) by allowing the prepolymer (A) to react with the amines (B) before dispersing the toner composition in the aqueous medium, or by dispersing the prepolymer (A) in the aqueous medium and then adding the amines (B) to cause the reaction on particle interfaces. In the above procedure, the urea-modified polyester is formed preferentially on the surface of the prepared toner particles, and the toner particles may have a concentration gradient in the inside.

[0065]

To emulsify and disperse an oil phase containing the dispersed toner composition into a water-containing liquid, a dispersing agent is used. Examples of the dispersing agent include, but are not limited to: anionic surfactants such as alkylbenzene sulfonates,  $\alpha$ -olefin sulfonates, phosphoric esters; cationic surfactants of amine salts such as alkylamine salts, amino alcohol fatty acid derivatives, polyamine fatty acid derivatives, imidazoline, and cationic surfactants of quaternary ammonium salts such as alkyltrimethylammonium salts, dialkyldimethylammonium salts, alkyl dimethylbenzylammonium salts, pyridinium salts, alkylisoquinolinium salts, and benzethonium chloride; nonionic surfactants such as fatty acid amide derivatives, polyhydric alcohol derivatives; and amphoteric surfactants, for example alanine, dodecyl di(aminoethyl) glycine, di(octylaminoethyl) glycine, and N-alkyl-N,N-dimethylammonium betaines.

[0066]

Notable effects of the surfactants may be obtained in a small

amount by using a surfactant having a fluoroalkyl group.

Preferred examples of fluoroalkyl-containing anionic surfactants are fluoroalkylcarboxylic acids each containing 2 to 10 carbon atoms and metallic salts thereof, disodium

- 5 perfluorooctanesulfonyl glutamate, sodium 3-[omega-fluoroalkyl(C6 to C11)oxy]-1-alkyl (C3 to C4)sulfonate, sodium 3-[omega-fluoroalkanoyl(C6-C8)-N-ethylamino]-1-propanesulfonate, fluoroalkyl(C11 to C20)carboxylic acids and metallic salts thereof, perfluoroalkyl carboxylic acids(C7 to C13) and metallic
- 10 salts thereof, perfluoroalkyl(C4 to C12)sulfonic acids and metallic salts thereof, perfluorooctanesulfonic acid diethanolamide, N-propyl-N-(2-hydroxyethyl)perfluorooctanesulfonamide, perfluoroalkyl(C6 to C10)sulfonamide propyl trimethyl ammonium
- 15 salts, perfluoroalkyl(C6 to C10)-N-ethylsulfonyl glycine salts, and monoperfluoroalkyl(C6 to C16)ethyl phosphoric esters.

- Such fluoroalkyl-containing anionic surfactants are commercially available under the trade names, for example, of
- 20 SURFLON S-111, S-112 and S-113 (from Asahi Glass Co., Ltd.), FLUORAD FC-93, FC-95, FC-98 and FC-129 (from Sumitomo 3M Limited), UNIDYNE DS-101 and DS-102 (from Daikin Industries, Ltd.), MEGAFAC F-110, F-120, F-113, F-191, F-812 and F-833 (from Dainippon Ink & Chemicals, Incorporated), EFTOP EF-102, 103, 104, 105, 112, 123A, 123B, 306A, 501, 201 and 204 (from JEMCO Inc.), and FTERGENT
- 25 F-100 and F-150 (from Neos Co., Ltd.).

[0067]

- Examples of cationic surfactants for use in the present invention include aliphatic primary, secondary and tertiary amic acids each having a fluoroalkyl group; aliphatic quaternary
- 30 ammonium salts such as perfluoroalkyl(C6-C10)sulfonamide propyltrimethylammonium salts; benzalkonium salts; benzethonium chloride; pyridinium salts; and imidazolinium salts. Such cationic surfactants are commercially available, for example,

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under the trade names of SURFLON S-121 (from Asahi Glass Co., LTD.), FLUORAD FC-135 (from Sumitomo 3M Limited), UNIDYNE DS-202 (from Daikin Industries, LTD.), MEGAFAC F-150, and F-824 (from Dainippon Ink & Chemicals, Incorporated), EFTOP EF-132 (from JEMCO Inc.), and FTERGENT F-300 (from Neos Co., Ltd.).

[0068]

In addition, an inorganic compound which is only slightly soluble in water, such as calcium phosphate, calcium carbonate, titanium oxide, colloidal silica and hydroxyapatite, may be also used as the dispersing agent.

Moreover, dispersed liquid droplets may be stabilized with polymer-based protection colloid. For the above purpose, the following substances may be used, for example; homopolymers or copolymers of acids such as acrylic acid, methacrylic acid,  $\alpha$ -cyanoacrylic acid,  $\alpha$ -cyanomethacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid, and maleic anhydride; hydroxyl-group-containing (meth)acrylic monomers such as  $\beta$ -hydroxyethyl acrylate,  $\beta$ -hydroxyethyl methacrylate,  $\beta$ -hydroxypropyl acrylate,  $\beta$ -hydroxypropyl methacrylate,  $\gamma$ -hydroxypropyl acrylate,  $\gamma$ -hydroxypropyl methacrylate, 3-chloro-2-hydroxypropyl acrylate, 3-chloro-2-hydroxypropyl methacrylate, diethylene glycol monoacrylic ester, diethylene glycol monomethacrylic ester, glycerol monoacrylic ester, glycerol monomethacrylic ester, N-methylolacrylamide, and N-methylolmethacrylamide; vinyl alcohol and ethers thereof such as vinyl methyl ether, vinyl ethyl ether, and vinyl propyl ether; esters of vinyl alcohol and a carboxyl-group-containing compound, such as vinyl acetate, vinyl propionate, and vinyl butyrate; acrylamide, methacrylamide, diacetone acrylamide, and methylol compounds thereof; acid chlorides such as acryloyl chloride, and methacryloyl chloride; and vinylpyridine, vinylpyrrolidone, vinylimidazole, ethyleneimine, and other vinyl monomers containing a nitrogen atom or having a nitrogen-containing

heterocyclic ring. Examples of the polymer substance also include polyoxyethylene compounds such as polyoxyethylene, polyoxypropylene, polyoxyethylene alkyl amines, polyoxypropylene alkyl amines, polyoxyethylene alkyl amides, polyoxypropylene alkyl amides, polyoxyethylene nonyl phenyl ether, polyoxyethylene lauryl phenyl ether, polyoxyethylene stearyl phenyl ester, and polyoxyethylene nonyl phenyl ester; and cellulose derivatives such as methyl cellulose, hydroxyethyl cellulose, and hydroxypropyl cellulose.

10 [0069]

When a calcium phosphate, and the like, that is soluble in acids or bases is used as the dispersion stabilizer, the calcium phosphate is removed from the fine particles by dissolving the calcium phosphate by using an acid such as hydrochloric acid and then washing the fine particles. Alternatively, the dispersion stabilizer may also be removed, for example, by decomposition using an enzyme.

When a dispersing agent is used, the dispersing agent may be allowed to remain on the surface of the toner particles, but is preferably removed by washing after completion of at least one of the extension reaction and crosslinking reaction from the viewpoint of toner charge properties.

[0070]

In addition, a solvent which is capable of dissolving the urea-modified polyester and/or the prepolymer (A) may be used in order to lower viscosity of the liquid containing the toner composition. Application of the solvent is preferable because a sharper particle diameter distribution is obtained. The solvent is preferably volatile with a boiling point of lower than 100 °C for easier removal. Examples of such solvents include toluene, xylenes, benzene, carbon tetrachloride, methylene chloride, 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate,



ethyl acetate, methyl ethyl ketone, and methyl isobutyl ketone. Each of these solvents can be used alone or in combination. Among the above compounds, aromatic hydrocarbon solvents such as toluene and xylene, and halogenated hydrocarbons, such as methylene chloride, 1,2-dichloroethane, chloroform and carbon tetrachloride, are preferred. The amount of the solvent is generally in the range of from 0 to 300 parts, preferably from 0 to 100 parts, and more preferably from 25 to 70 parts, relative to 100 parts of the prepolymer (A). The solvent, if any, is removed by heating at atmospheric pressure or under reduced pressure after completion of the extension- and/or crosslinking reaction.

[0071]

Reaction time for extension and/or crosslinking between the reactive modified polyester and the amine (B) as a crosslinking agent and/or extension agent is appropriately set depending on the reactivity based on the combination of the isocyanate structure of the prepolymer (A) and the amine (B), and ranges generally from 10 minutes to 40 hours and preferably from 2 to 24 hours. Reaction temperature is generally chosen in the range of from 0 °C to 150 °C and preferably from 40 °C to 98 °C. Where necessary, a known catalyst such as dibutyltin laurate and dioctyltin laurate may be used.

[0072]

(Irregular shape forming step)

To obtain a non-spherical shape, a highly viscous aqueous solution (aqueous phase) to which a thickening agent, an active agent, and the like are added is mixed with an emulsified dispersion liquid (oil phase), and the mixture is passed through a device such as a homo mixer or Ebara Milder, to impart shearing force, thereby deforming emulsified particles by using a viscosity difference between the oil phase and the aqueous phase. As conditions for deforming the shape, a method of adjusting the

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viscosity difference between the oil phase and the aqueous phase by adjusting concentration and temperature of a hydrophilic organic solvent in the oil phase, and the thickening agent, the active agent and temperature in the aqueous phase may be adopted.

5 As the hydrophilic organic solvent, although conventionally known solvents are usable, ethyl acetate is preferable in particular. Measurement of organic solvent concentration is controllable by a method of adjusting shearing force of the device, for example, by a shape of the treatment device, treatment time, number of  
10 treatment cycles, or treatment temperature.

[0073]

For removing the organic solvent from the obtained emulsified dispersion, a method of completely removing the organic solvent in liquid drops by evaporation by gradually increasing  
15 temperature of the entire system may be employed. Alternatively, the organic solvent may be removed by spraying the emulsified dispersion in a dry atmosphere, thereby completely removing a water-insoluble organic solvent in liquid drops to form toner fine particles while removing a water-based dispersing agent by  
20 evaporation. As the dry atmosphere to which the emulsified dispersion is sprayed, a heated gas, such as air, nitrogen, a carbon dioxide gas, a combustion gas, particularly various air flows heated to a temperature higher than a boiling point of a solvent having a highest boiling point are generally used. Object  
25 quality is sufficiently obtained by short time treatment by using a spray drier, a belt drier, a rotary kiln, or the like.

[0074]

When particle size distribution during emulsification dispersion is wide and washing and drying processes are carried  
30 out while maintaining the particle size distribution, particle size distribution may be classified into desired particle size distribution. In the classification operation, fine particle fractions may be removed by using a cyclone, a decanter,

centrifugal separation, or the like in a liquid. The classification operation may be carried out on fine particles after drying, but the operation is preferably carried out in a liquid in terms of efficiency. Obtained unnecessary fine particles or coarse particles are returned again to a kneading step, and may be used for formation of particles. In the case, the fine particles or the coarse particles may be in a wet condition.

The used dispersant is preferably removed from the obtained dispersion liquid, and preferably removed simultaneously with the classification operation described previously.

The obtained fine particles of toner after drying are mixed with particles of different kinds, such as fine particles of a releasing agent, fine particles of a charge control agent, fine particles of a plasticizer, and particles of a colorant. By giving mechanical impact force to the mixture of particles, the mixture is fixed and uniformly blended with the toner particles on a surface thereof, and thus the particles of different kinds may be prevented from separating from obtained surfaces of the complex particles.

Specific means includes a method of applying impact force to the mixture by a blade rotating at high speed, and a method of supplying the mixture in high-speed flow and accelerating the mixture to cause the particles or the complex particles to collide with an appropriate collision plate. Devices therefor, angmill (manufactured by Hosokawa Micron Corporation), a modified I-type mil (manufactured by Nippon Pneumatic MFG., Co., Ltd.) in which pulverizing air pressure is reduced, a hybridization system (manufactured by Nara Machine Corporation), Kryptron System (manufactured by Kawasaki Heavy Industries, Ltd.), and an automatic mortar.

[0075]

(Two-component carrier)

When the toner of the present invention is used for a two-component developer, the toner may be used by being mixed with a magnetic carrier, and a content ratio of the carrier in the developer and the toner is preferably 1 to toner 10 parts by weight of the toner to 100 parts by weight of the carrier. As the magnetic carrier, conventionally known carriers may be used, such as particles of iron, ferrite, magnetite, and a magnetic resin carrier having a particle diameter of 20 to 200  $\mu\text{m}$ . As a coating material, an amino resin, for example, a urea-formaldehyde resin, a melamine resin, a benzoguanamine resin, a urea resin, a polyamide resin, an epoxy resin, and the like are cited. Further, a polyvinyl and polyvinylidene system resin, for example, an acrylic resin, a polymethyl methacrylate resin, a polyacrylonitrile resin, a polyvinyl acetate resin, a polyvinyl alcohol resin, a polyvinyl butyral resin, a polystyrene-based resin such as a polystyrene resin and styrene-acrylic copolymer resin, a halogenated olefine resin such as polyvinyl chloride, a polyester-based resin such as a polyethylene terephthalate resin and a polybutyrene terephthalate resin, a polycarbonate resin, a polyethylene resin, a polyvinyl fluoride resin, a polyvinylidene fluoride resin, a polytrifluoroethylene resin, a polyhexafluoropropylene resin, a copolymer of vinylidene fluoride and an acrylic monomer, a copolymer of vinylidene fluoride and vinyl fluoride, fluoroterpolymers, such as a terpolymer of tetrafluoroethylene, vinylidene fluoride and a non-fluorinated monomer, a silicone resin, and the like may be used. Conductive powder and the like may be contained in a coating resin when necessary. As the conductive powder, metal powder, carbon black, titanium oxide, tin oxide, zinc oxide, and the like may be used. Such conductive powder has preferably an average particle diameter of 1  $\mu\text{m}$  or smaller. When an average particle diameter is larger than 1  $\mu\text{m}$ , control of electric resistance is difficult.

The toner of the present invention may be used also as

one-component magnetic or nonmagnetic toner without using a carrier.

[0076]

The tone of the present invention is used for a process cartridge of the present invention, characterized by integrally supporting a photoconductor and at least one means selected from a group of a charge means, a development means, and a cleaning means, and the process cartridge is freely attachable to and detachable from an image forming apparatus body.

Fig. 4 shows a schematic structure of an image forming apparatus having the process cartridge of the present invention.

In the drawing, a reference numeral (20) indicates an entire process cartridge, (21) indicates a photoconductor, (22) indicates a charge means, (23) indicates a development means, and (24) indicates a cleaning means. According to the present invention, a plurality of components, such as the photoconductor (21), the charge means (22), the development means (23), and the cleaning means (24), are integrally formed as a process cartridge, and the process cartridge is configured to be attachable to and detachable from an image forming apparatus body, such as a copier and a printer.

[0077]

In the image forming apparatus having the process cartridge of the present invention, the photoconductor rotates at predetermined peripheral speed. The photoconductor receives uniform charging of positive or negative predetermined electric potential on the peripheral surface by the charge means in a rotation process, and subsequently, receives image exposure light from an image exposure means, such as slit exposure or laser beam scanning exposure. Thus, electrostatic latent images are sequentially formed on the circumferential surface of the photoconductor, and then, toner development of the formed electrostatic latent images are performed by the development

means. The developed toner images are sequentially transferred by a transfer means to a transfer material synchronized with rotation of the photoconductor and fed between the photoconductor and the transfer means from a paper feed part. The transfer material having received the transferred images is separated from the photoconductor surface, and introduced to an image fixing means to fix the images, and then output from the device as a printed copy. Remaining toner on the surface of the photoconductor after image transfer is removed and cleaned by the cleaning means, destaticized, and repetitively used for image formation thereafter.

[0078]

[Embodiment]

The present invention is further described according to embodiment in the following, but the present invention is not limited thereto. In the following, "part" represents a part by weight.

The toner used in each example is collectively shown in Table 1.

<Example 1>

(Synthesis of organic fine particle emulsion)

Preparation example 1

In a reaction container equipped with a stirrer and a thermometer, 754 parts of water, 13 parts of a sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid (ELEMNOL RS-30, manufactured by Sanyo Chemical Industries, Ltd.), 83 parts of styrene, 83 parts of methacrylic acid, 110 parts of butyl acrylate, and 1 part of ammonium persulfate are fed, and stirred at 400 rpm for 15 minutes to obtain a white emulsion. The emulsion was heated up to an inner temperature of 75 °C, and reacted for 5 hours. Further, 30 parts of a 1 % aqueous solution of ammonium persulfate were added, and aged at 75 °C for 5 hours to obtain an aqueous dispersion [polymer fine particle dispersion]

1] of a vinyl resin (copolymer of styrene-methacrylic acid-butyl acrylate-sodium salt of sulfuric acid ester of ethylene oxide adduct of methacrylic acid). A volume average particle diameter of [fine particle dispersion 1] measured with LA-920 was 0.10  $\mu\text{m}$ .

5 A part of [fine particle dispersions 1] was dried, and resin component was isolated. Tg of the resin component was 57 °C.

[0079]

(Preparation of aqueous phase)

Preparation example 2

10 990 parts of water, 80 parts of [fine particle dispersion 1], 40 parts of a 48.5 % aqueous solution (ELEMNOL MON-7: manufactured by Sanyo Chemical Industries, Ltd.) of sodium dodecyldiphenyl ether disulfonate, and 90 parts of ethyl acetate are mixed and stirred to obtain milky liquid. The obtained liquid  
15 is [aqueous phase 1].

[0080]

(Unmodified polyester)

Preparation example 3

In a reaction vessel equipped with a condenser tube, a  
20 stirrer, and a nitrogen gas introducing tube, 570 parts of ethyleneoxide 2 mol adduct of bisphenol A, 217 parts of terephthalic acid, and 2 parts of dibutyltin oxide are added. The mixture was polycondensed at 230 °C under normal pressure for 8 hours, subsequently, reacted at a reduced pressure of 10 to 15  
25 mmHg for 5 hours, and cooled to 110 °C. Further, 18 parts of trimellitic anhydride was added, and reaction is carried out for  
2 hours to obtain unmodified polyester (a).

[0081]

(Preparation example of prepolymer)

30 Preparation example 4

In a reaction vessel equipped with a condenser tube, a stirrer, and a nitrogen gas introducing tube, 343 parts of ethyleneoxide 2mol adduct of bisphenol A, 100 parts of

isophthalic acid, 66 parts of terephthalic acid, and 2 parts of dibutyltin oxides are placed. The mixture was reacted at 230 °C under normal pressure for 8 hours, and further reacted for 5 hours while carrying out dehydration under a reduced pressure of 10 to 15 mmHg. After cooling to 110 °C, 32 parts of trimellitic anhydride was added to the reaction mixture, and reacted for 2 hours. Subsequently, the reaction mixture was cooled to 80 °C, reacted with 17 parts of isophorone diisocyanate in ethyl acetate for 2 hours, and a isocyanate group containing prepolymer (1) was obtained.

[0082]

(Preparation example of ketimine compound)

Preparation example 5

In a reaction vessel equipped with a stirring rod and a thermometer, 170 parts of isophoronediamine and 70 parts of methyl ethyl ketone were fed, reaction was performed at 50 °C for 5 hours to obtain a ketimine compound (1).

[0083]

(Preparation example of toner)

Preparation example 6

In a beaker, 14.3 parts of prepolymer (1), 55 parts of unmodified polyester (a), and 78.6 parts of ethyl acetate were placed, stirred, and dissolved. Subsequently, 10 parts of rice wax (melting point 83 °C), 7 parts of carbon black #44 (manufactured by Mitsubishi Chemical Corporation) as a releasing agent were added, stirred at 12,000 rpm by using a TK-type homo mixer at 60 °C for 5 minutes, and dispersed by using a bead mill at 20 °C for 30 minutes. A resultant solution is toner material solution (1).

[0084]

Next, 306 parts of aqueous phase 1 described above was placed in the beaker. Subsequently, the above toner material solution



(1) and 2.7 part of ketimine compound (1) were added with stirring at 12,000rpm by using a TK-type homo mixer for urea reaction. A particle diameter and particle size distribution were observed with an optical microscope, and when a particle diameter is large, stirring revolution speed is raised to 14,000 rpm and the stirring was continued for further 5 minutes. When a particle diameter is small, the stirring was changed to 10,000 rpm and the stirring was again conducted. Subsequently, the mixed solution was placed in a flask equipped with a paddle stirring rod which may stir at peripheral speed of 5 m/s or more and a thermometer, temperature is increased up to 45 °C, fast stirring was carried out at peripheral speed of 6 m/s for 2 hours, and spindle-shaped matrix toner particles were obtained. A starch solution is fed to control viscosity of the aqueous phase during stirring at 1,000 to 50,00CP. Stirring time is extended when the spindle shape is insufficient. Then, the solvent was removed at 50 °C or less under reduced pressure over 1.0 hour, and filtration, washing, and drying were carried out. Subsequently, air classification was performed to obtain spindle-shaped base particles.

Next, 100 parts of obtained base particles and 0.25 part of charge controlling agent (Bontron E-84 manufactured by Orient Chemical Industries, Ltd.) were fed in a Q Mixer (manufactured by Mitsui Mining Co., Ltd.). Peripheral speed of a turbine blade is set to 50 m/sec, and 5 cycles of 2 minutes of operation and 1 minute of pause, and total treatment time was 10 minutes.

Further, 0.5 part of hydrophobic silica (H2000 manufactured by Clariant Japan Co., Ltd.) was added, peripheral speed was set to 15 m/sec, and 5 cycles of 30 seconds of mixing and 1 minute of a pause were carried out to obtain cyan toner. Subsequently, 0.5 part of hydrophobic silica and 0.5 part of hydrophobing titanium oxide were mixed by using a Henschel Mixer to obtain toner (1) according to the present invention. The evaluation results are shown in Table 2.

[0085]

<Example 2>

(Preparation example of prepolymer)

Preparation example 7

5 In a reaction vessel equipped with a condenser tube, a stirrer, and a nitrogen gas introducing tube, 856 parts of ethyleneoxide 2 mol adduct of bisphenol A, 200 parts of isophthalic acid, 20 parts of terephthalic acid, and 4 parts of dibutyltin oxide were added, and reacted at 250 °C under normal  
10 pressure for 6 hours, further reacted while carrying out dehydration under a reduced pressure of 50 to 100 mmHg for 5 hours. After cooling to 160 °C, 18 parts of trimellitic anhydride was added to the reaction mixture, and reacted for 2 hours. Subsequently, after cooling to 80 °C, the reaction mixture was  
15 reacted with 17 parts of isophorone diisocyanates in ethyl acetate for 2 hours to obtain an isocyanate group containing prepolymer (2).

[0086]

(Preparation example of toner)

20 Preparation example 8

15.4 parts of the above prepolymer (2), 50 parts of unmodified polyester (a), and 95.2 parts of ethyl acetate were placed in a beaker, stirred and dissolved. Subsequently, 20 parts of carnauba wax (molecular weight 1,800, acid value 2.5,  
25 penetration 1.5mm/40 °C) and 7 parts of carbon black were added, stirred at 10,000 rpm by using a TK-type homo mixer at 85 °C dispersed, emulsified, and stirred by using a bead mill similar to example 1 to obtain base toner particles (2). The evaluation results are shown in Table 2.

30 Next, toner (2) was prepared similar to example 1 except that the base particles and a charge controlling agent (Bontron E-89 manufactured by Orient Chemical Co., Ltd.) were used.

[0087]

<Example 3>

(Preparation example of unmodified polyester)

Preparation example 9

5 Similar to the above example, 589 parts of ethyleneoxide 2  
mol adduct of bisphenol A, 464 parts of terephthalic acid  
dimethyl ester, and 3 parts of dibutyltin oxides were added, and  
polycondensed at 230 °C under normal pressure for 6 hours.

Subsequently, the mixture was reacted under a reduced pressure of  
10 to 15 mmHg for 5 hours to obtain unmodified polyester (b).

10 [0088]

(Preparation example of toner)

Preparation example 10

15 15.3 parts of the prepolymer (1), 63.6 parts of the  
unmodified polyester (b), 40 parts of toluene, and 40 parts of  
ethyl acetate were placed in a beaker, stirred, and dissolved.  
Subsequently, 10 parts of rice wax and 7 parts of carbon black  
(Regal 400R: manufactured by Cabot Corp.) were added, stirred at  
12,000 rpm by using a TK-type homo mixer at 60 °C, and then  
dispersed by using a bead mill at 25 °C for 30 minutes. Finally,  
20 1.1 parts of diphenylmethane diisocyanates was added as an  
extender, and dissolved. The reaction mixture is toner material  
solution (3).

Operation was carried out similar to example 1 and the toner  
material solution (3) was added with stirring at 12,000 rpm by  
25 using a TK-type homo mixer, and then stirred for 10 minutes.  
Subsequently, the mixed solution is moved to a flask equipped  
with a paddle stirring rod and thermometer, and temperature is  
increased up to 50 °C over 30 minutes for urethane reaction. The  
dispersion liquid was stirred at peripheral speed of 20.5 m/s in  
30 a homo mixer (manufactured by Tokushyu Kika Kogyo Co., Ltd.) for  
25 minutes, and the solvent was removed at 50 °C or less. After  
filtrating, washing, and drying were performed, air  
classification was performed to obtain spindle-shaped base

particles according to the present invention. Toner 3 was obtained similar to example 1. The evaluation results are shown in Table 2.

[0089]

5 <Example 4>

(Preparation example of prepolymer)

Preparation example 11

In a reaction vessel equipped with a condenser tube, a stirrer, and a nitrogen gas introducing tube, 755 parts of ethyleneoxide 2 mol adduct of bisphenol A, 195 parts of isophthalic acid, 15 parts of terephthalic acid, and 4 parts of dibutyltin oxides were placed, reacted at 220 °C under normal pressure for 8 hours, and further reacted while carrying out dehydration under a reduced pressure of 50 to 100 mmHg for 5 hours. After cooling to 110 °C, 10 parts of trimellitic anhydride was added to the reaction mixture, and reacted for 2 hours. Subsequently, the reaction mixture was cooled to 80 °C, and then reaction was performed with 170 parts of isophorone diisocyanate in an ethyl acetate for 2 hours to obtain isocyanate group containing prepolymer (3).

[0090]

(Preparation example of toner)

Preparation example 12

In a beaker, 15.4 parts of the prepolymer (3), 50 parts of the unmodified polyester (a), and 95.2 parts of ethyl acetate were placed, stirred, and dissolved. Subsequently, 20 parts of carnauba wax (molecular weight 1,800, acid value 2.5, penetration 1.5 mm/40 °C) and 7 parts of carbon black (MOGULL L: manufactured by Cabot Corp.) were placed, and stirred at 12,000 rpm by using a TK-type homo mixer at 85 °C, and dissolved uniformly, then dispersed by using a bead mill at 15 °C for 50 minutes. The dispersion is toner material solution (4).

The toner material solution (4) was placed in a beaker with

stirring at 12,000 rpm by using a TK-type homo mixer similar to example 1. After stirring for 10 minutes, 2.7 parts of ketimine compound (1) was added for elongation reaction. Subsequently, the mixed solution was moved to a flask equipped with a stirring rod and a thermometer, stirred at 300 rpm at 40 °C for 2 hours to produce spindle-shaped base toner particles. Then the solvent was removed at 40 °C over 1 hour, filtration, washing, and drying were carried out to obtain spindle-shaped base particles (4). Concentration of an emulsified dispersion liquid at the time was 13 %. Toner 4 was obtained similar to example 1. The results are shown in Table 2.

[0091]

<Comparative example 1>

(Synthesis of toner binder)

395 parts of ethyleneoxide 2 mol adduct of bisphenol A and 166 parts of isophthalic acid were polycondensed by using 2 parts of dibutyltin oxide as a catalyst to obtain a comparison toner binder (comparison 1).

[0092]

(Preparation of toner)

In a beaker, 100 parts of the comparison toner binder (comparison 1), 180 parts of ethyl acetate solution, 4 parts of copper phthalocyanine blue pigment, and a 10 % hydroxyapatite suspension (Supertite 10 manufactured by Nippon Chemical Industrial Co., Ltd.) and sodium dodecylbenzenesulfonate as dispersing agents were placed, and stirred at 50°C and at 10,000 rpm by using a TK-type homo mixer, uniformly dissolved and dispersed. Subsequently, toner particles were prepared similar to example 1, except that the solvent was removed over 1 hour in a desolventization step. Then, 0.3 part of hydrophobic titanium oxide and 0.3 part of hydrophobic silica were mixed to 100 parts of toner particles in a Henschel mixer. The evaluation results of obtained toner are shown in Table 2.

[0093]

<Comparative example 2>

(Synthesis of toner binder)

In a reaction vessel equipped with a condenser tube, a  
5 stirrer, and a nitrogen gas introducing tube, 343 parts of  
ethyleneoxide 2 mol adduct of bisphenol A, 166 parts of  
isophthalic acid, and 2 parts of dibutyltin oxide were placed,  
and reacted at 230 °C under normal pressure for 8 hours, and  
further reacted under a reduced pressure of 10 to 15 mmHg for 5  
10 hours. After cooling to 80 °C, 14 parts of toluene diisocyanate  
were placed in toluene and reaction was carried out at 110 °C for  
5 hours, followed by removal of the solvent to obtain a  
urethane-modified polyester was obtained. Similar to example 1,  
363 parts of ethyleneoxide 2 mol adduct of bisphenol A and 166  
15 parts of isophthalic acid were polycondensed to obtain an  
unmodified polyester. A comparative toner binder (comparison 2)  
was obtained by dissolving and mixing 350 parts of the  
urethane-modified polyester and 650 parts of the unmodified  
polyester in toluene, and removing the solvent thereafter.

20 [0094]

(Preparation of toner)

100 parts of comparative toner binder (2), 2 parts of  
chromium complex of salicylic acid (E-81 manufactured by Orient  
Chemical Co., Ltd.) as a charge controlling agent, and 4 parts of  
25 copper phthalocyanine blue pigment were made into toner by a  
following method. First, preliminary mixing was carried out by  
using a Henschel mixer, then kneading was carried out in a  
continuous kneading machine. Subsequently, after pulverizing in a  
jet pulverizer, classification was carried out in a pneumatic  
30 classifier. A total of 100 parts of toner particles was mixed  
with 0.3 part of hydrophobic titanium oxide and 0.3 part of  
hydrophobic silica in a Henschel mixer. The evaluation results of  
obtained toner are shown in Table 2.

[0095]

<Comparative example 3>

Polyester resin (bisphenol resin, manufactured by Kao Corp.;  
Mn: 6,000, Mw: 70,000, Tg: 64 °C) 90 parts

5 Carbon black (BP1300, manufactured by Cabot Corp.) 10 parts

Rice wax (melting point: 82 °C) 10 parts

Diethylether/dichloromethane mixed solution (50:50) 300 g

The above components were mixed and dispersed by using a ball  
mill for 10 hours. An obtained dispersion liquid was poured into  
10 400 g of 2 % aqueous solution of gum arabic, and dispersed for 3  
minutes by using a homo mixer. Then, the dispersion was poured  
into 2,000 g of pure water, and held at 80 °C in a water bath,  
stirred by a Three-one motor and held for 4 hours. Thus,  
irregular particles without regularity having an average particle  
15 diameter of 6.0  $\mu$ m and recessed portions were obtained.

Temperature of the suspension in the state was increased up to  
98 °C, held at the temperature for 1 hour, and spherical  
particles having a substantially same particle diameter is  
obtained, followed by adding a charge controlling agent in a Q  
20 mixer similar to example 1 to obtain comparative toner 3. The  
evaluation results are shown in Table 2.

[0096]

<Comparative example 4>

[Mixing step]

25 Styrene n-butyl acrylate resin (coporimerization ratio: 55:45,  
Mn: 3,100, Mw: 8,200, prepared by solution polymerization)

Carbon black (manufactured by Cabot Corp.) 5 parts

Polypropylene (molecular weight: approximately 8,000,  
30 manufactured by Mitsui Chemicals, Inc.) 5 parts

The above components were kneaded and dispersed in a Banbury  
mixer (manufactured by Kobe Steel, Ltd.). 100 parts of the  
dispersion is put into 400 parts of ethyl acetate, and stirred at





A measurement method of Tg is outlined. A thermal analyzer DSC-60 manufactured by Shimadzu Corporation was used as a device for measuring Tg.

Approximately 5 mg of test sample was first placed in a test sample container made of aluminum, and the container was put on a holder unit and set in an electric furnace. The test sample was heated from room temperature to 150 °C at a heating rate of 10 °C/min under an nitrogen atmosphere, and cooled to room temperature at a heating rate of 10 °C/min. The test sample was heated again to 150 °C at a heating rate of 10 °C/min, and subjected to DSC measurement. A contact between a tangential line of an endothermic curve in the vicinity of Tg and a baseline was read by using the DSC-60 analysis system, and defined as Tg.

[0099]

15 (2) Acid value and hydroxyl value

The test sample was determined according to a method specified in JIS K 0070. However, when the sample was not dissolved, dioxane or tetrahydrofuran was used as a solvent.

[0100]

20 (3) Powder fluidity

Bulk density of the test sample was measured by using a Hosokawa Micron Powder Tester. Toner with a larger bulk density has a larger flowability. The flowability was evaluated according to following four steps.

25 X: Less than 0.25

△: 0.25 to 0.30

O: 0.30 to 0.35

◎: 0.35 or more

[0101]

30 (4) Heat-resistant storage stability

Toner was stored at 50 °C for 8 hours, followed by sieving through 42-meshe sieve for 2 minutes, a residual ratio on a wire

COPY

net was defined as heat-resistant storage stability. Toner having smaller residual ratio is toner with larger heat-resistant storage stability. The heat-resistant storage stability was evaluated according to following four steps.

- 5       X: 30 % or more  
       △: 20 to 30%  
       ○: 10 to 20%  
       ⊙: Less than 10 %

[0102]

10   (5) Lowest fixing temperature

A copying test was carried out by using a modified copier imagio NEO 450 manufactured by Ricoh Co., Ltd. as a fixing roller, with Type 6200 paper manufactured by Ricoh Co., Ltd. set thereto. Temperature of the fixing roller at which a remaining ratio of  
15 image density of a fixed image was 70 % or more after rubbing the fixed image with a pad was defined as lowest fixing temperature.

\* A fixing unit was modified, and an Fe material of 0.34-mm thick was used for a metallic cylinder of the fixing roller. Contact pressure was set to  $1.0 \times 10^5$  Pa.

20       [0103]

(6) Hot offset generating temperature (HOT)

Fixing was evaluated similar to the lowest fixing temperature, and presence or absence of hot offset to a fixed image was visually evaluated. Fixing roll temperature at which the hot  
25 offset was generated was defined as hot offset generating temperature.

[0104]

(7) Charging stability

Amounts of charge at low temperature/low humidity and high  
30 temperature/high humidity were measured by a blow-off method, and a range of fluctuation was evaluated. Iron powder coated with a silicone resin was used as a carrier, and measurement was carried out under conditions of 30 °C, 90% and 10 °C 30 %. A small change

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is required.

X: Unusable

△: Difference is large.

○: Difference is slightly large.

5      ◎: Difference is few and stable.

[0105]

(8) Cleanability

A surface of a latent image carrier immediately after cleaned by a cleaning blade was visually observed. Toner adhering to the carrier surface was taken to a transparent tape, and stuck on  
10 white paper. Image density was measured from above by using a Macbeth densitometer.

[0106]

(9) Durability

15      Number of copies for which a clear copy image is obtained was investigated.

[0107]

(10) Gradation

Gradation was evaluated by using a ten-step chart.

20      [0108]

Recycling efficiency evaluation

<Preparation of developer>

A developer was prepared by mixing and sufficiently shaking 50 parts of classified toner having a particle diameter of 10 to  
25 11  $\mu\text{m}$  and 950 parts of carrier coated with a silicon resin (KR250 manufactured by Shin-Etsu Chemical Co., Ltd. core carrier: 70  $\mu\text{m}$ ). Image evaluation of 100,000 sheets was performed by using the developer and a modified copier imagio NEO 450 manufactured by Ricoh Co., Ltd. equipped with a recycling  
30 system.

[0109]

(11) Content of fine powder

Particle size distribution of the toner was determined by

using a Coulter Counter TA-2 (manufactured by Coulter Electronics, Inc.) after 100,000-sheet copy. In the procedure, a 1 % NaCl solution was used as an electrolyte, and Drywell was used as a dispersant. A percentage by number of fine powder having a particle diameter of 5.04  $\mu\text{m}$  was determined based on data of particle size distribution output by a computer.

[0110]

(12) Toner aggregation

Toner in a developing unit was sampled after 100,000 copies to investigate presence or absence of agglomerates of toner. A case that the agglomerates of toner were hardly observed was evaluated as "O", a case that some agglomerates of toner were observed but in practical use level was evaluated as " $\Delta$ ", and a case that many toner agglomerates were observed in a problematic use level was evaluated as "X".

[0111]

(13) Flowability of toner

Toner in the developing unit was sampled after 100,000 copies, and flowability of the toner was visually observed. A satisfactory case was evaluated as "O", a case that flowability was somewhat poor but in a practical use level was evaluated as " $\Delta$ ", and a case that flowability was remarkably inferior and problematic in practical use was evaluated as "X".

[0112]

(14) Durability of toner

Early image density of solid part and mage density after 100,000-sheet copy were evaluated according to following criteria.

O: There is little deterioration in density and a clear image is obtained.

$\Delta$ : There is deterioration in density but in an allowable level.

X: There is deterioration in density and in an unallowable

level.

[0113]

(15) Image scumming evaluation

5 A scumming level of an image is determined in a durability evaluation.

Rank 1: There is no generation of scumming and the image is clear.

Rank 2: There is a little scumming observed but in an allowable level from a viewpoint of image quality.

10 Rank 3: There is scumming observed in an unallowable level from a viewpoint of image quality.

[0114]

(16) Image evaluation

An abnormal image is checked in the durability evaluation.

15 Check items: black spot, image blur, generation of carrier adhesion.

[0115]

[Table 1]

	Binder used	Prepolymer	Acid value	Yg (°C)	Others
Example 1	Polyester a	Prepolymer 1	8	55	
Example 2	Polyester a	Prepolymer 2	9	58	
Example 3	Polyester b	Prepolymer 1	16	48	
Example 4	Polyester a	Prepolymer 3	13	49	
Comp. example 1	Comp. 1 polyester	—	35	72	Dissolving-suspending method
Comp. example 2	Comp. 2 polyester	Urethane-modified	14	75	Pulverizing method
Comp. example 3	Polyester	—	12	58	Dissolving-suspending method
Comp. example 4	Styrene-acryl	—	2.5	51	Dissolving-suspending method

[0116]

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[Table 2-1]

	SF-1	Circu- larity	DV/Dn	VAP diameter	2 $\mu$ m or smaller (%)	Lowest fixing temp. (°C)	Hot offset (°C)	Charge stability	heat- resistant storage stability	Powder fluidity
Example 1	155	0.94	1.15	4.7	5.5	150	220	○	○	◎
Example 2	195	0.92	1.26	5.5	20.0	150	220	○	◎	◎
Example 3	171	0.94	1.14	4.9	7.5	160	230	○	◎	○
Example 4	165	0.93	1.05	4.1	5.0	140	220	○	○	○
Comp. example 1	115	0.97	1.38	7.0	18.0	175	210	×	○	○
Comp. example 2	160	0.94	1.45	5.5	23.0	185	195	○	○	×
Comp. example 3	125	0.97	1.15	6.8	11.5	160	180	○	△	△
Comp. example 4	140	0.95	1.06	4.8	6.8	165	185	○	△	×

Remarks: VAP diameter: Volume average particle diameter

[0117]

[Table 2-2]

	Content of powder (%)	Toner aggregation (%)	Durability	Flowability	Scumming	Abnormal image, state	Cleanabilit y	Gradation
Example 1	18	○	○	○	1	None	0.04	8
Example 2	16	○	○	△	1	None	0.1	9
Example 3	24	○	○	○	2	None	0.03	8
Example 4	15	○	○	○	1	None	0.08	10
Comp. example 1	38	△	×	○	3	Defective cleaning	0.02	8
Comp. example 2	20	×	×	△	2	None	0.05	8
Comp. example 3	32	△	△	△	1	Defective cleaning	0.15	9
Comp. example 4	16	×	○	△	3	None	0.1	9

5

[0118]

As shown in the tables, the comparative examples 2 and 4 have smaller particle diameters and a higher aggregation degrees, and

flowability is poor, which generates scumming.

The comparative examples 1, 2, and 4 have smaller SF-1, are substantially spherical, and show insufficient blade cleanability.

Further, the comparative examples 1 and 2 have a higher Tg,  
5 and show higher lowest fixing temperature.

The comparative example 3 has an irregular shape with rugged portions, high fine powder content, and does not satisfy the toner aggregation, the durability, the flowability, and the cleanability.

10 The comparative example 4 contains a styrene acrylic resin, and therefore has a high lowest fixing temperature although having a small particle diameter.

On the other hand, examples 1 to 4 have little fine powder generation in the apparatus, and show no problem in the image and  
15 contamination in the apparatus. In particular, examples 1 to 4 excel in blade cleanability due to high SF-1.

However, when SF-1 is excessively high, example 2 has a tendency to generate fine powder, and slightly low cleanability.

Example 4 excels in fixing effect and gradation when a  
20 particle diameter is small and  $D_v/D_n$  is small.

[0119]

[Effects of the Invention]

As is clear from the above detailed and specific description, dry type toner of the present invention has following effect.

25 The toner used for an image forming method employing a toner recycling system contains at least a modified polyester resin, a colorant, and a releasing agent, characterized in that a surface of the toner is coated with a fine particle polymer, a volume average particle diameter ( $D_v$ ) of the toner is 4.0 to 6.0  $\mu\text{m}$ , a  
30 ratio  $D_v/D_n$  of the volume average particle diameter ( $D_v$ ) to a number average particle diameter ( $D_n$ ) is 1.00 to 1.30, and a shape factor SF-1 of the toner is 140 to 200. The toner excels in recycling efficiency, causes neither charge deterioration due to

oozing out of wax to a surface nor deterioration in image sharpness due to agglomeration, invites less transfer residual toner in an apparatus using blade cleaning, and yields a high-definition image.

5 [Brief Description of the Drawings]

[Fig. 1] Fig. 1 shows a digital copy type image forming apparatus as an example of an image forming apparatus used in the present invention.

[Fig. 2] Fig. 2 is an enlarged schematic diagram showing a principal part of an example of the image forming apparatus according to the present invention.

[Fig. 3] Fig. 3 is an enlarged schematic diagram of an example of a recycling device of the image forming apparatus according to the present invention.

15 [Fig. 4] Fig. 4 shows a schematic structure of an example of an image forming apparatus having a process cartridge according to the present invention.

[Reference Numerals]

1	Photoconductor	2	Charger
20	3 Exposure means	4	Development means
	5 Transfer means	5a	Transfer belt
	6 Cleaning means	6a	Cleaning blade
	6b Brush roller	6c	Eject port
	7 Document placing table	8	Reading means
25	9 Sheet feeding device	10	Fixing means
	11 Cleaning means	12	Tank
	13 Recycling device	13a	Conveyance pipe
	13b Rotation screw conveyor	20	Process cartridge
	21 Photoconductor	22	Charge means
30	23 Development means	24	Cleaning means
	40 Development tank	41	Toner hopper
	42 Permeability sensor	43	Replenishment roller
	44 Stirring member	45	Paddle wheel



46 Development roller

47 Development doctor

[Name of Document] Abstract of the Disclosure

[Abstract]

[Objectives of the Invention]

5 To provide toner and a developer which do not cause  
deformation and destruction of toner when employed in a toner  
recycling system, produces only a small change in a surface state  
of toner, do not cause deterioration in durability of developer,  
fogging, deterioration in image density, scumming, an  
10 environmental variation in toner, and the like, and is capable of  
yielding excellent image quality, and an image forming apparatus  
and an attachable and detachable process cartridge. Further, to  
provide toner and a developer capable of yielding high-definition  
image quality having excellent fine dot reproducibility, and high  
15 reliability in cleaning in particular. Also, to provide toner and  
a developer having an excellent low temperature fixing property.  
Moreover, to provide toner and a developer capable of satisfying  
the above objects. Further, to provide toner which has excellent  
transfer efficiency, leaves little transfer residual toner, and  
20 is capable of yielding a high-definition image.

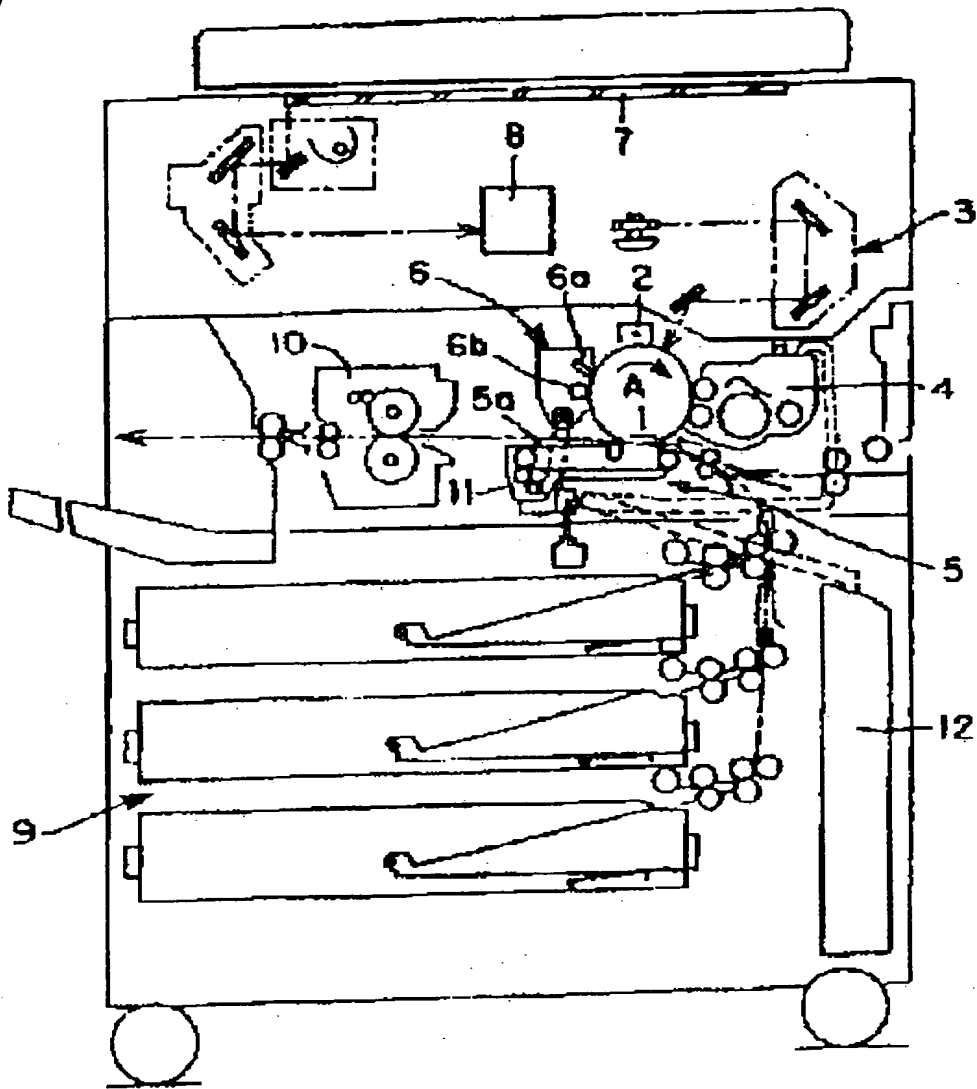
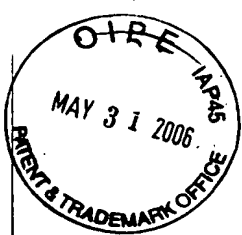
[Means for Achieving the Objectives]

Toner used for an image forming method employing a toner  
recycling system, and containing at least a modified polyester  
resin, a colorant, and a releasing agent, characterized in that a  
25 surface of the toner is coated with a fine particle polymer, a  
volume average particle diameter ( $D_v$ ) of the toner is 4.0 to 6.0  
 $\mu\text{m}$ , a ratio  $D_v/D_n$  of the volume average particle diameter ( $D_v$ )  
to a number average particle diameters ( $D_n$ ) is 1.00 to 1.30, and  
a shape factor SF-1 of the toner is 140 to 200.

30 [Selected Drawing] Fig. 2

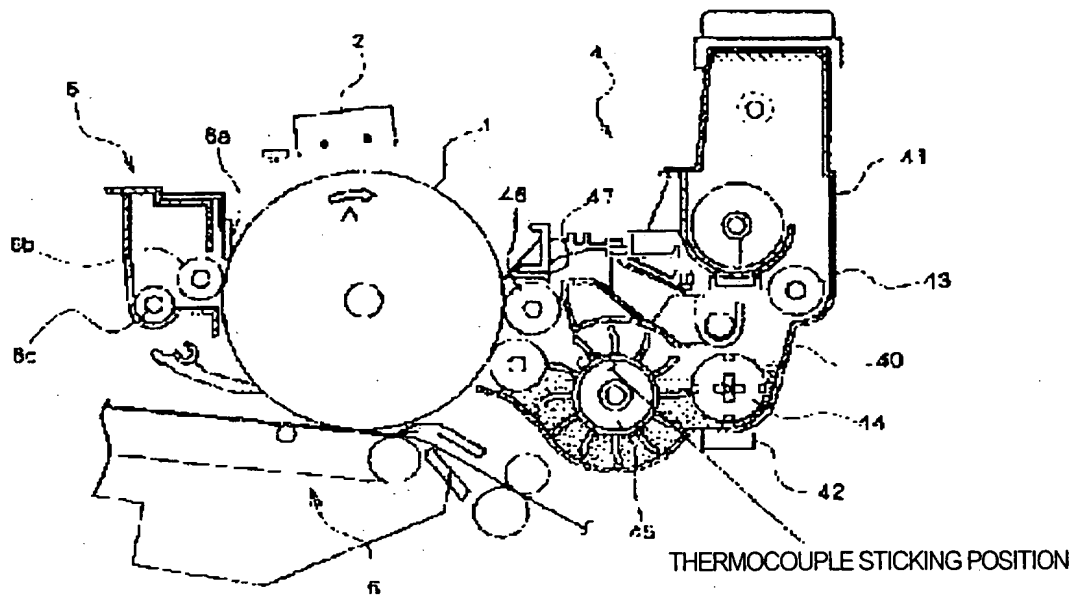
[Name of Document] Drawing

[Fig. 1]

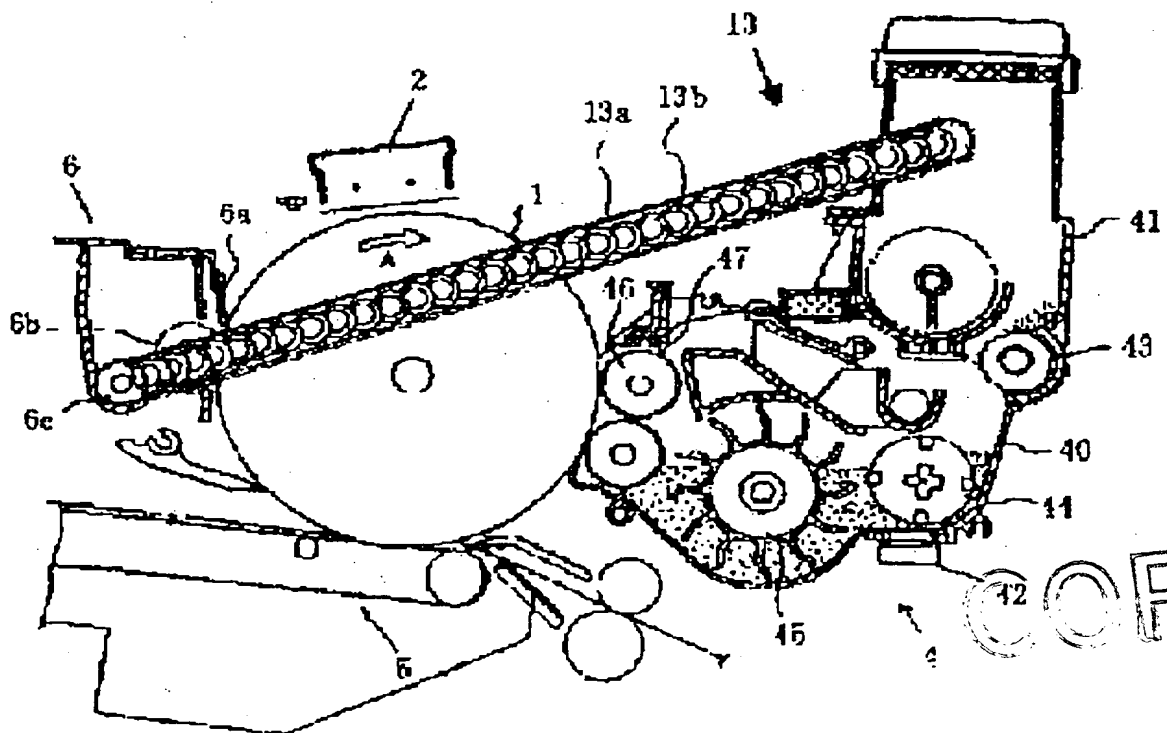


COPY

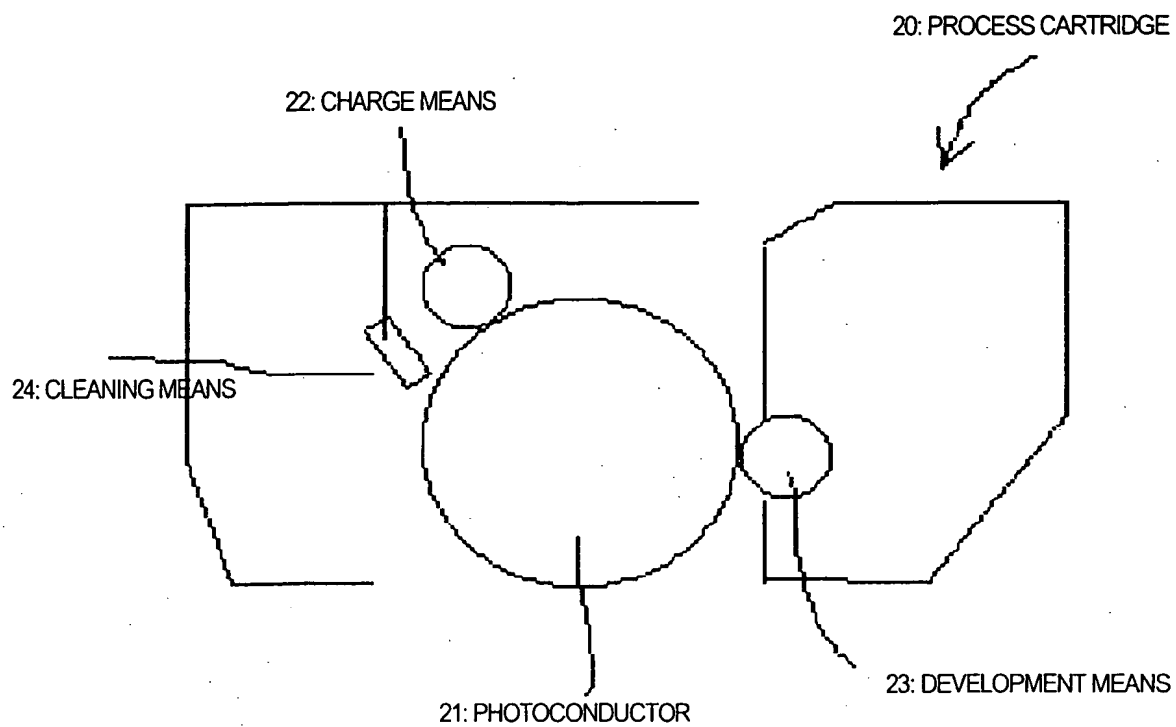
[Fig. 2]



[Fig. 3]



[Fig. 4]



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